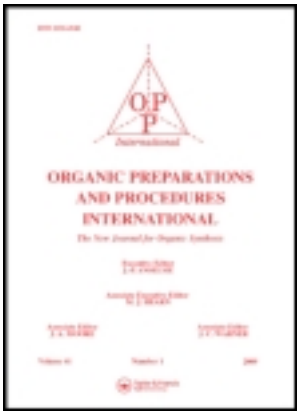


Organic Preparations and Procedures International: The New Journal for Organic Synthesis

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/uopp20

Recent Progress in the Use of N-Halo Compounds in Organic Synthesis

Hojat Veisi [a b], Ramin Ghorbani-Vaghei [c] & Mohamad Ali Zolfigol [c]

[a] Department of Chemistry, Payame Noor University (PNU), Iran

[b] Young Reaserchers Club, Kermanshah Branch, Islamic Azad University, Kermanshah, Iran

[c] Department of Organic Chemistry, Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran

Version of record first published: 16 Nov 2011.

To cite this article: Hojat Veisi , Ramin Ghorbani-Vaghei & Mohamad Ali Zolfigol (2011): Recent Progress in the Use of N-Halo Compounds in Organic Synthesis, Organic Preparations and Procedures International: The New Journal for Organic Synthesis, 43:6, 489-540

To link to this article: http://dx.doi.org/10.1080/00304948.2011.629553

Organic Preparations and Procedures International, 43:489–540, 2011

ISSN: 0030-4948 print / 1945-5453 online
DOI: 10.1080/00304948.2011.629553

Recent Progress in the Use of *N*-Halo Compounds in Organic Synthesis

Hojat Veisi,[1,2] Ramin Ghorbani-Vaghei,[3] and Mohamad Ali Zolfigol[3]

[1]Department of Chemistry, Payame Noor University (PNU), Iran
[2]Young Reaserchers Club, Kermanshah Branch, Islamic Azad University, Kermanshah, Iran
[3]Department of Organic Chemistry, Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran

Recent Progress in the Use of *N*-Halo Compounds in Organic Synthesis

Hojat Veisi,[1,2] Ramin Ghorbani-Vaghei,[3] and Mohamad Ali Zolfigol[3]

[1]Department of Chemistry, Payame Noor University (PNU), Iran
[2]Young Reaserchers Club, Kermanshah Branch, Islamic Azad University, Kermanshah, Iran
[3]Department of Organic Chemistry, Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran

Introduction and background of the *N*-Halo Compounds

The exploitation of reagents for the development new synthetic methods is an art and constitutes a challenging process in organic chemistry. Consequently, considerable efforts have been made over the years to devise newer reagents that can minimize the drawbacks of those presently in use. For this purpose, a large number of *N*-halo reagents have been extensively developed for use in organic synthesis. These include *N*-haloamines, *N*-haloamides, *N*-haloimides, *N*-haloureas, *N*-halosaccharins, *N*-halosulfonamides, *N*-halosulfonimides, *etc*.

N-Halo compounds are versatile reagents and have been employed as potentially reactive intermediates that are widely used in organic synthesis. Although the scope of the application of such compounds is so wide that all *N*-halo reagents cannot be considered within the framework of a single review article, we have decided to introduce them briefly and believe that this may be useful to achieve new ideas and applications. It should be noted that the chemistry of *N*-halo reagents has been the subject of several review articles.[1–9] Numerous new data have subsequently been reported in the literature and these are summarized in the present review. Some specific features of *N*-halo reagents such as the high activity of the *N*-X bond and the various modes of fission of this bond determine their wide application in organic synthesis.

All *N*-halo reagents are easy to handle and all of the halogen is consumed, not half as in the case of elemental halogens. Depending on the conditions, a number of highly

Received January 12, 2010; in final form August 19, 2011.
Address correspondence to Hojat Veisi, Department of Chemistry, Payame Noor University, 19395-4697 Tehran, Islamic Republic of Iran. E-mail: hojatveisi@yahoo.com or Ramin Ghorbani-Vaghei, Department of Organic Chemistry, Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran. E-mail: rgvaghei@yahoo.com

reactive intermediates can be formed: halogen radicals, halogen cations, halogen anions, *N*-radicals, *N*-cations, *N*-anions, *etc*. Consequently, *N*-halo reagents have the potential to promote important reactions such as halogenations, oxidation, protection and deprotection as well as formation of C-X, C-O and C=O bonds.

In addition to the numerous organic and inorganic halogenating agents, *N*-halo reagents play an especially important role as Lewis acid catalysts in the chemistry of heterocyclic compounds. Some of the *N*-halo reagents which are presented in *Schemes 1–4* are reviewed in this article.

I. *N*-Halo Compounds as Halogenating Agents

1. Halogenation of Aromatic Compounds

Halogenated aromatic compounds are a useful class of intermediates as they are precursors to a number of organometallic species useful in the synthesis of natural products and pharmaceutically important compounds. The manufacture of a range of bulk and fine chemicals, including flame retardants, disinfectants, antibacterials, and antiviral drugs, involve bromination.[10–14]

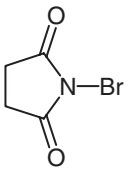
The introduction of halogens into aromatics rings by electrophilic substitution is an important synthetic procedure. Chlorine and bromine are reactive toward aromatic hydrocarbons, but Lewis acid catalysts are normally used to achieve desirable rates.[15,16] Some of the reagents reported for bromination[17–21] are often hazardous, very toxic, expensive, not readily available, need to be freshly prepared, or require drastic conditions or prolonged reaction times,[17,18] and tedious work-up. Thus, milder, more selective, non-hazardous, and inexpensive reagents are still in demand. Thus, in the search for new and safer reagents, *N*-halo reagents have been used as mild and selective halogenation agents in organic reactions.

N-Halosulfonamides have been widely used in organic synthesis. Recently some new *N*-halosulfonamides have been reported as chemoselective halogenating agents for a broad range of organic compounds. Ghorbani-Vaghei and Jalili have described *N,N,N′,N′*-tetrabromobenzene-1,3-disulfonamide (TBBDA) and poly(*N*-bromobenzene-1,3-disulfonamide) (PBBS) for the bromination of activated aromatic compounds in good yields. *N,N′*-Diiodo-*N,N′*-ethanediyl*bis*(4-methylbenzene)sulfonamide and *N,N′*-dibromo-*N,N′*-ethanediyl*bis*(4-methylbenzene)sulfonamide [BNBTS] has been used as a novel halogenating agent for the halogenation of some aromatic compounds in high yields (*Scheme 5*).[22–24]

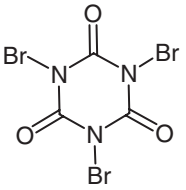
In 1993, Auerbach and co-workers reported that 1,3-dibromo-5,5-dimethylhydantoin in aqueous NaOH can be used as an efficient reagent for the bromination of activated benzoic acids. They also showed that DBH gave better yield than NBS (*Scheme 6*).[25]

Studies showed that the rate of the bromination of various aromatic compounds substituted with electron donating groups with DBH, is considerably enhanced in the presence of trimethyltrifluoromethanesulfonate (TMSOTf) (Scheme 7).[26]

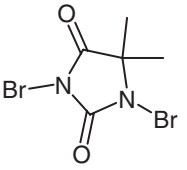
The authors explained activation of DBH in the presence of TMSOTf *via* bromination of triflate, as a reactive intermediate (Scheme 8).



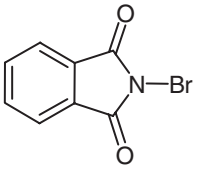
N-Bromosuccinimide
(NBS)



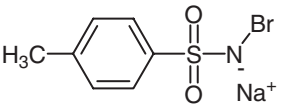
Tribromoisocyanuric Acid
(TBCA)



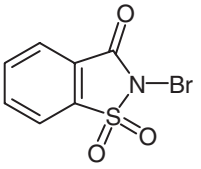
1,3-dibromo-5,5-imethylhydantoin
(DBH)



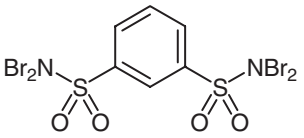
N-Bromophthalimide
(NBPI)



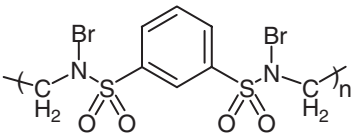
N-Bromo-para-toluene sulfonamide
sodium salt (Bromoamine T)



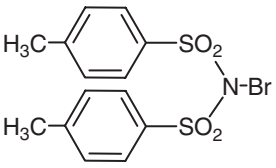
N-Bromosaccharin
(NBSa)



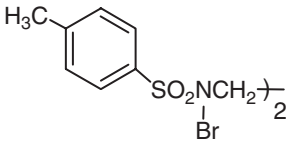
N,N,N′,N′-Tetrabromobenzene-
1,3-disulfonamide
(TBBDA)



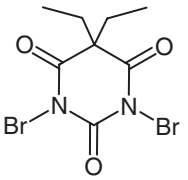
Poly(*N*-bromo benzene-1,3-disulfonamide)
(PBBS)



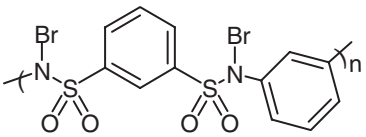
N-Bromo *bis*(*p*-toluenesulfonyl)amine
(NBBTA)



N,N′-Dibromo-*N,N*′-1,2-ethanediyl
bis(p-toluenesulfonamide)
(BNBTS)

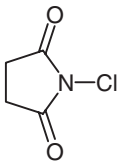


1,3-Dibromo-5,5-diethylbarbituric acid

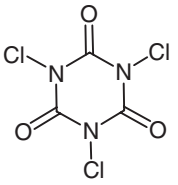


Poly(*N,N*′-dibromo-*N*-phenylbenzene-
1,3-disulfonamide)
(PBPS)

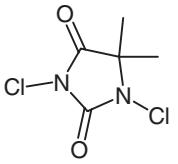
Scheme 1
N-Bromo Reagents



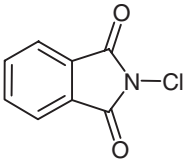
N-Chlorosuccinimide
(NCS)



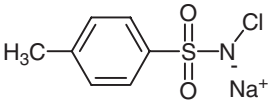
Trichloroisocyanuric Acid
(TCCA)



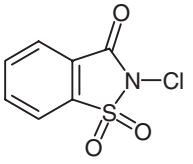
1,3-dichloro-5,5-imethylhydantoin
(DCH)



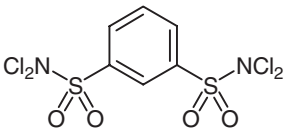
N-Chlorophthalimide
(NCPI)



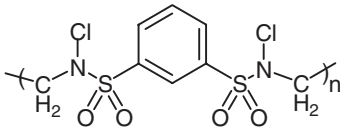
N-Chloro-para-toluene sulfonamide
sodium salt (Chloramine T)



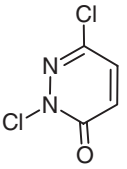
N-Chlorosaccharin
(NCSa)



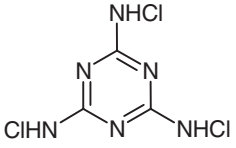
N,N,N',N'-Tetrachlorobenzene-
1,3-disulfonamide
(TCBDA)



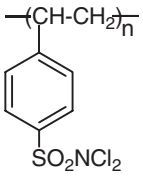
Poly *N*-chloro benzene-1,3-disulfonamide
(PCBS)



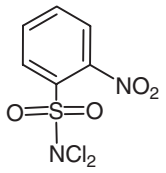
2,6-Dichloropyridazin-3(2H)-one



Trichloromelamine
(TCM)

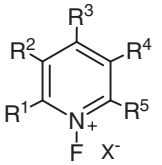


Poly [4-vinyl-*N,N'*-dichloro benz-
enesulphonamide]

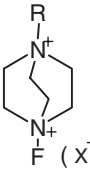


2-Nitro-*N,N'*-dichloro-benzensulfonamide
(2–$NsNCl_2$)

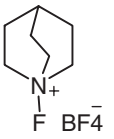
Scheme 2
N-Chloro Reagents



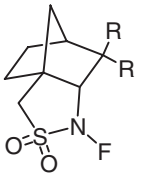
N-Flouro pyridinium salts



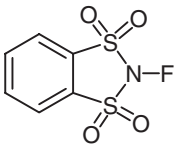
1-Alkyl-4-fluro-1,4-diaza bicyclo[2,2,2] octane



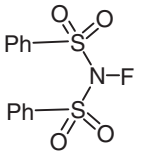
N-Fluoroquinuclidinium tetrafluoroborate



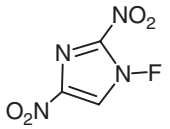
N-Fluorocamphorsultam



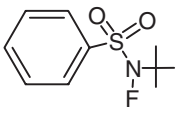
N-Fluoro-o-benzene disulfonimide



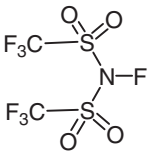
N-Fluorobenzensulfinimide



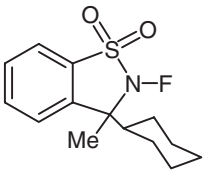
N-Flouro-2,4-dinitro imidazole



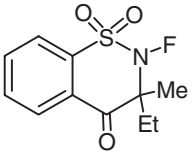
N-t-Butyl-*N*-Flurobenzen sulfonamide



N-Flourobis[(trifluoromethyl) sulfonyl]imide



N-Fluoro-3-cyclohexyl-3-methyl-2,3-dihydro benzo[1,2-d]isothiazole-1,1-dioxide



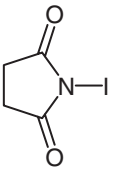
N-Fluoro-3-ethyl-3-methyl-1,1-dioxo-2,3-dihydro-1 6-benzo[e] 1,2-thiazin-4-one

Scheme 3
N-Fluoro Reagents

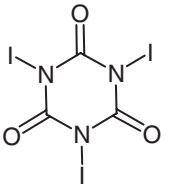
Similarly, Eguchi and co-workers used DBH in the presence of organic and inorganic acids with *pKa* values less than -2, to obtain the monobrominated products in excellent yields. Very good yields were achieved even with aromatic substrates having electron-withdrawing substituents (*e. g*. NO_2); in some cases, a catalytic amount of acids was sufficient (*Scheme 9*).[27]

In 2005, Tsuboi *et al*. found that DBH (0.5–0.55 eq.) is able to act as an efficient reagent for the conversion of phenols and polyphenols to their corresponding *ortho*-monobromo derivatives in good to excellent yields (*Scheme 10*).[28]

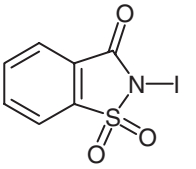
They also studied the regioselective bromination of pyrogallol derivatives by DBH, which gave regioselective single monobromo compounds in 1.5 h at room temperature (*Scheme 11*).[29]



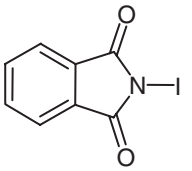
N-Iodosuccinimide
(NIS)



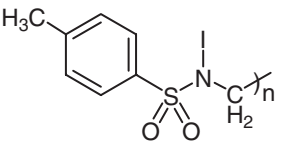
Triiodoisocyanuric Acid
(TICA)



N-Iodosaccharin
(NISa)

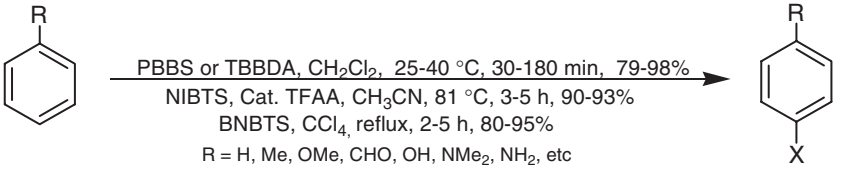


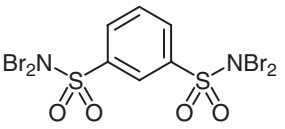
N-Iodophthalimide
(NIPI)



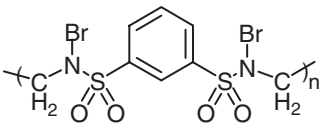
N,N'-Diiodo-*N,N*'-1,2-ethanediyl
bis(p-toluene sulfonamide)
(NIBTS)

Scheme 4
N-Iodo Reagents

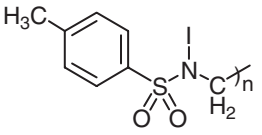




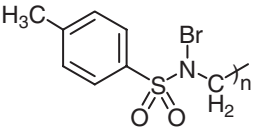
N,N,N',N'-Tetrabromobenzene-
1,3-disulfonamide
(TBBDA)



Poly *N*-bromo benzene-1,3-disulfonamide
(PBBS)

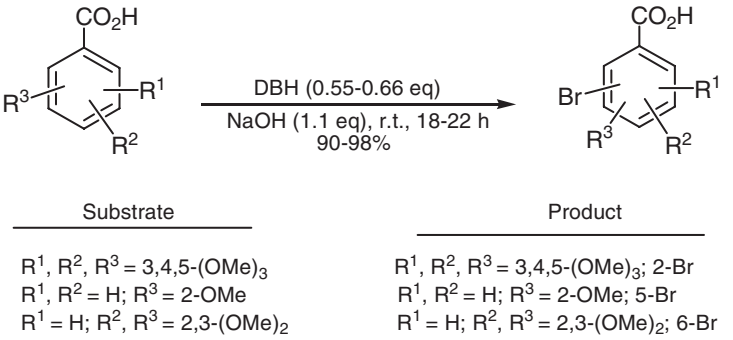


N,N'-Diiodo-*N,N*'-1,2-ethanediyl
bis(*p*-toluenesulfonamide)
(NIBTS)

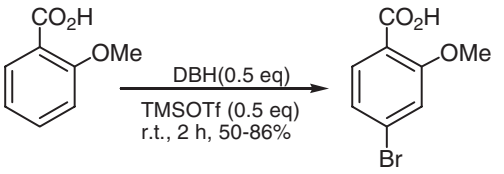


N,N'-Dibromo-*N,N*'-1,2-ethanediyl
bis(*p*-toluenesulfonamide)
(BNBTS)

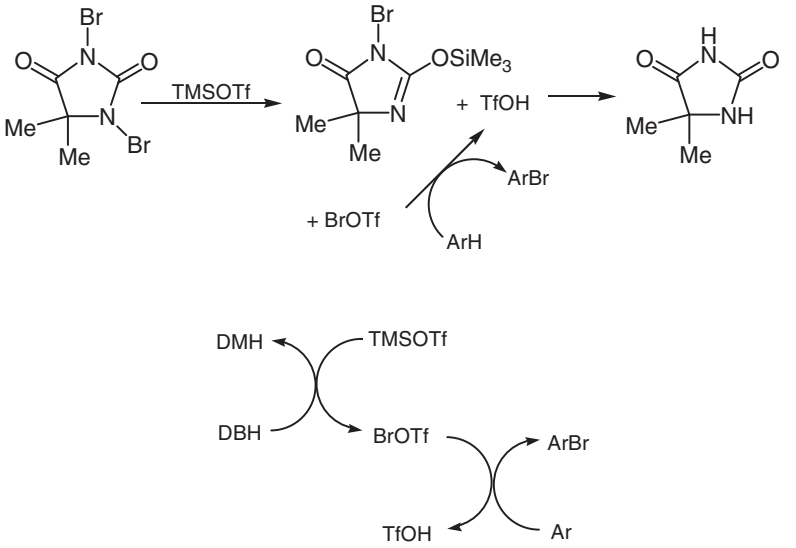
Scheme 5
Halogenation of Aromatic Compounds



Scheme 6
Bromination of Activated Benzoic Acids by DBH

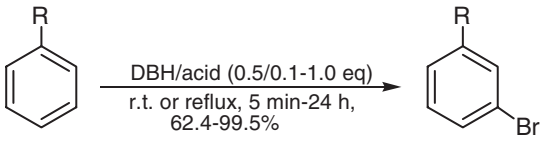


Scheme 7
Bromination of Various Aromatic Derivatives



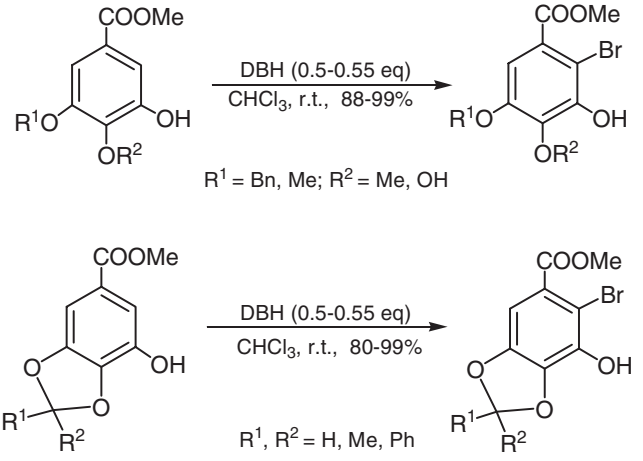
Scheme 8
Activation of DBH in the Presence of TMSOTf

In 2006, Azarifar *et al*. showed that DBH is able to promote the bromination of sydnones to their 4-bromo substituted congeners in excellent yields in DMF at room temperature (*Scheme 12*).[30]

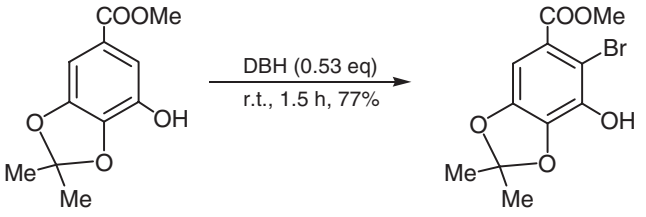


R	H_2SO_4	CF_3SO_3H
NO_2	75%	87%
CF_3	81%	86%
OMe	97%	97%
CO_2Me	71%	76%

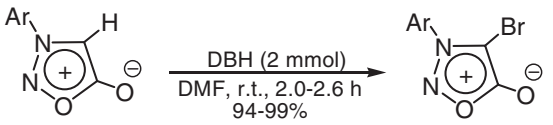
Scheme 9
Monobromination of Various Aromatic Compounds with DBH in the Presence of Organic and Inorganic Acids



Scheme 10
Bromination of Phenols and Polyphenols

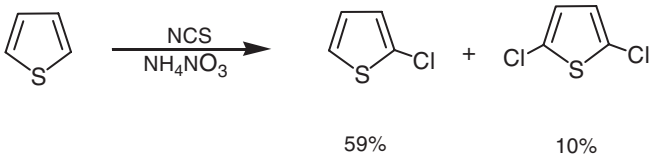


Scheme 11
Bromination of Pyrogallol Derivatives by DBH



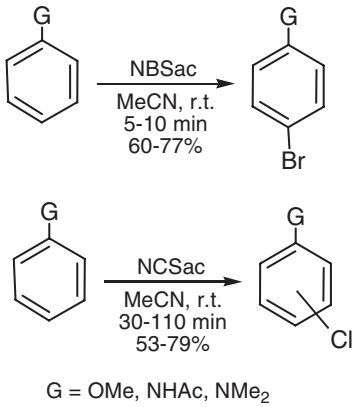
Scheme 12
Bromination of Sydnones to their 4-Bromo Derivatives

Acid-sensitive substrates are efficiently chlorinated by NCS in the presence of mildly acidic ammonium nitrate; for example in the case of thiophene (*Scheme 13*), a mixture of 2-chlorothiophene (59% yield) and 2,5-dichlorothiophene (10% yield) was obtained.[31]



Scheme 13
Chlorination of Thiophene with NCS

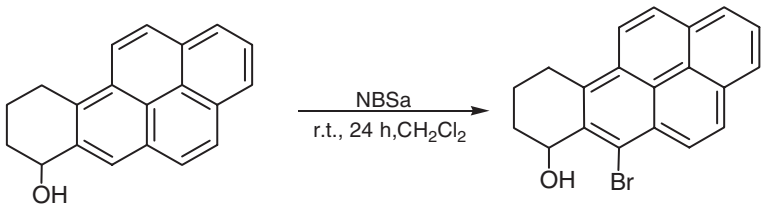
NCSac and NBSac were successfully applied for the halogenation of electron-rich aromatic compounds (anisole, acetanilide, *N*,*N*-dimethylaniline). The reaction with *N*-bromosaccharin gives *para*-substituted compounds only, whereas *N*-chlorosaccharin produces *ortho* and *para* mixtures (*para* isomer predominantly, *ca.* 4–5: 1) (*Scheme 14*).[32]



Scheme 14
Chlorination and Bromination of Electron-rich Aromatic Compounds with NBSac and NCSac

Bromination of 7,8,9,10-tetrahydrobenzo[*a*]pyren-7-ol was selectively carried out with NBSac (*Scheme 15*).[33]

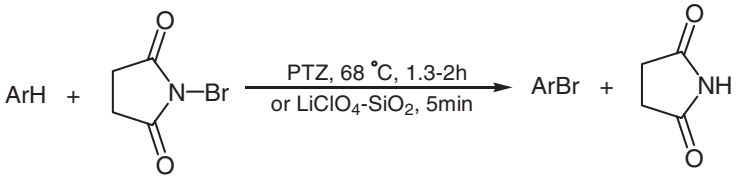
Regioselective monobrominated aromatic compounds were obtained in excellent yields (86–98%) using NBS in the presence of phosphotungstic acid supported on zirconium (PTZ)



product ratio : 66% (6-Bromo)/34% (other)

Scheme 15
Bromination of 7,8,9,10-Tetrahydrobenzo[*a*]pyren-7-ol with NBSac

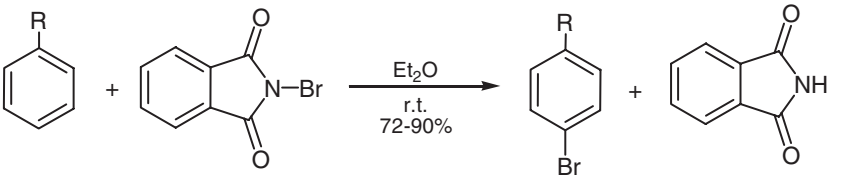
as a novel heterogeneous catalyst.[34] When $LiClO_4$-SiO_2 was applied as catalyst, reaction time was reduced to 5 minutes (*Scheme 16*).[35]



ArH = toluene, anisol, *N,N*-dimethylaniline, etc.

Scheme 16
Bromination of Aromatic Compounds with NBS

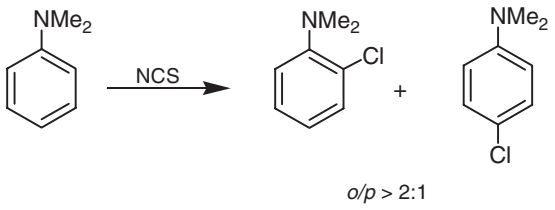
Reaction of substituted benzene rings with NBP, under neutral conditions, gave the corresponding bromo derivatives with a complete preference for the formation of *para* over the *ortho* isomers (*Scheme 17*).[36]



R = OCH_3, NHAc, NEt_2, OH, $CONH_2$

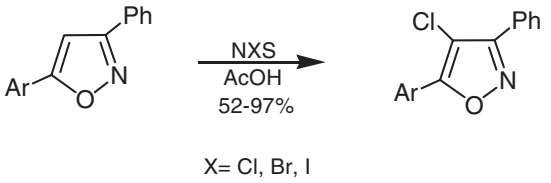
Scheme 17
Bromination of Substituted Benzene Rings with NBP

Aromatic chlorinations are usually carried out with elemental chlorine, sulfuryl chloride, chlorine(I) oxide, or hypochlorites.[37] In the search for new and safer reagents, NCS has been examined. The treatment of reactive aromatic compounds, such as *N*-alkylanilines, with NCS in hot benzene gave a mixture of *o*- and *p*-chloroanilines in ratio exceeding 2:1 (*Scheme 18*). The results were interpreted as arising from a rearrangement of intermediate *N*-chloro isomers.[38,39] Difficulties in obtaining monochlorinated products in acceptable yields in the reaction of deactivated anilines were obviated by the use of dipolar aprotic solvent such as acetonitrile.[40]



Scheme 18
Chlorination of *N*-Alkylanilines with NCS

The chlorination of heterocyclic systems with two heteroatoms and substituted at the 3- and 5-positions yields ring-chlorinated products selectively. The chlorination of 3,5-diarylisoxazoles with NCS in refluxing acetic acid afforded the 4-chloro derivatives (*Scheme 19*).[41] In the cases of electron-withdrawing substituents or a methyl group on the aryl group, the addition of a catalytic amount of sulfuric acid was required for efficient chlorination.



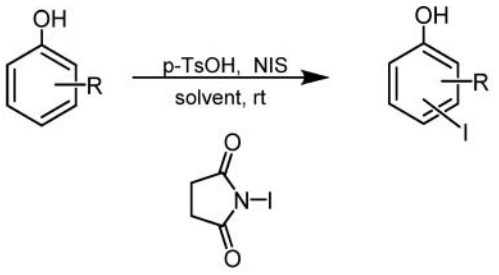
Scheme 19
Chlorination of Heterocyclic Systems with Two Heteroatoms

Iodination of phenols furnishes important synthetic intermediates[43] which are useful in a variety of palladium-catalysed and copper(I)-assisted reactions, such as the Heck, Stille and the Ullmann reactions.[44–46] Iodophenols are also constituents of various naturally occurring biologically active compounds, especially those of marine sponge metabolites.[47] Recentely, Bovonsombat *et al*. has reported a mild and highly regioselective monoiodination of phenol and analogues in high to excellent yields at room temperature with a combination of stoichiometric *p*-toluenesulfonic acid and *N*-iodosuccinimide (*Scheme 20*).[48]

Laulo *et al.* have shown that *N*-fluoro-2,4-dinitroimidazole can fluorinate several class of polycyclic aromatic hydrocarbons (PAHs). All fluorinated PAHs were obtained under reflux conditions in a few days (*Scheme 21*).[49]

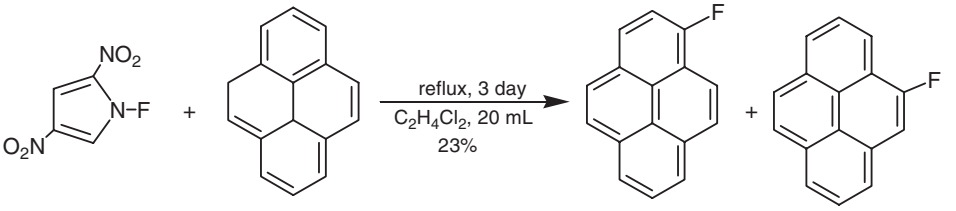
Banks *et al*. reported the preparation of some *N*-fluoro reagents,[50–52] which have been used for the fluorination of various organic compounds (*Scheme 22*).

Zupan *et al.* have described a regioselective method for the fluorination of dibenzofuran diphenyl ether and biphenyl with various *N*-fluoro agents. *Scheme 23* shows a typical experiment for the fluorination of dibenzofuran by three different types of *N*-fluoro reagents.[53]

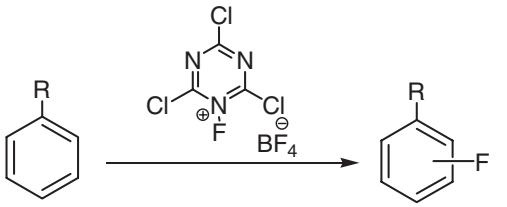


R = H, 2,3-C_4H_4, 3,4-C_4H_4, 2-OCH_3, 2-Br, 2-Cl, 4-Cl, 2-CH_3, 4-CH_3, 2-$COCH_3$, 2-CO_2CH_3

Scheme 20
Iodination of Phenol Derivatives with NIS



Scheme 21
Fluorination Several Class of Polycyclic Aromatic Hydrocarbons (PAHs)

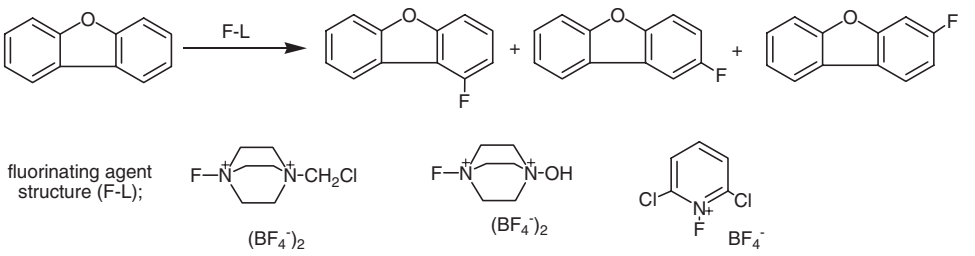


R = -NO_2, -Cl, -OMe

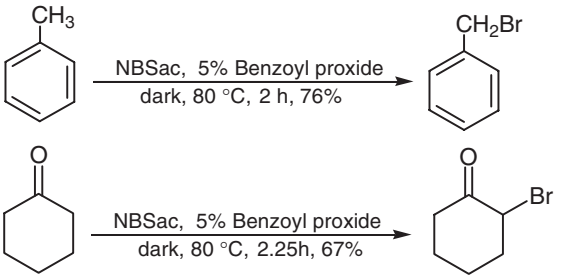
Scheme 22
Fluorination of Various Organic Compounds

2. Halogenation of Benzylic and Allylic Compounds,

The regioselective bromination of benzylic and allylic positions is a useful transformation in organic synthesis. The use of molecular bromine in preparative chemistry is a serious cause of concern due to its toxicity and corroding properties. Therefore, in 1942, Ziegler used NBS for benzylic bromination in CCl_4.[54] Sanchez and Fomarola reported benzylic and α- bromination with *N*-bromosaccharin in CCl_4 (*Scheme 24*).[55,58] These brominations are radical types reactions, which are either photo-initiated or promoted by addition of benzoyl



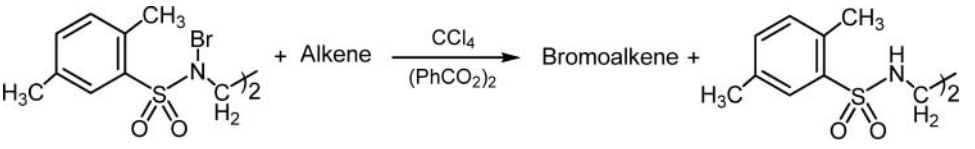
Scheme 23
Fluorination of Dibenzofuran Diphenylether and Biphenyl with Different *N*-Fluoro Agents



Scheme 24
Benzylic Bromination using *N*-Bromosaccharin

peroxide. Carbon tetrachloride has proven to be a useful solvent for the bromination of a wide range of compounds, and reports on its use still appear frequently.[56,57]

Bromination of allylic compounds have been described by with *N,N′*-dibromo-*N,N′*-ethanediyl*bis*(2,5-dimethylbenzene)sulfonamide (*Scheme 25*).[59]

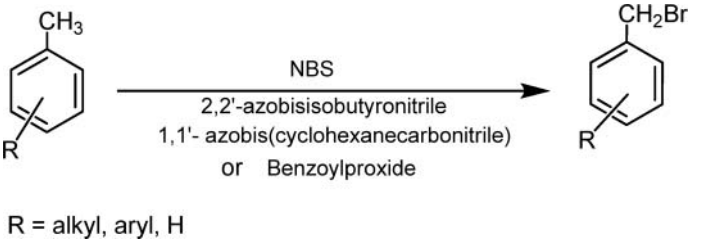


Cyclohexene	3-Bromocyclohexene	1 h 60%
1,5-Cyclooctadiene	3,5-Dibromo-1,5-cyclooctadiene	1 h 65%
2-Heptene	4-Bromo-2-heptene	1 h 73%
2-Methyl acrilic acid	2-(Bromomethyl)acrylic acid	6 h 74%

Scheme 25
Brominaion of Allylic Compounds

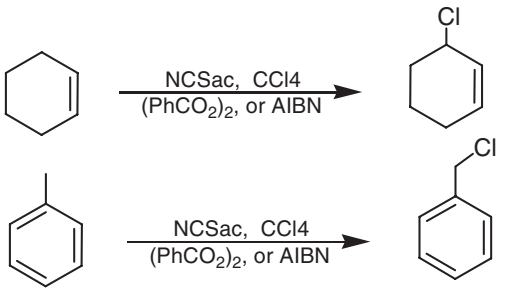
A variety of benzylic brominations were performed by using *N*-bromosuccinimide in (trifluoromethyl)benzene with photochemical activation in the presence of azo*bis*isobutyronitrile, or azo*bis*(cyclohexanecarbonitrile), or benzoyl peroxide as the radical initiator. This system provides a clean, rapid, and high-yielding reaction with

replacement of conventional solvents, such as CCl_4, by the less-toxic (trifluoromethyl)benzene (*Scheme 26*).[60]



Scheme 26
Benzylic Brominations using *N*-Bromosuccinimide

Bachhawat and co-workers described an allylic and benzylic chlorination of organic compounds with NCSac and benzoyl peroxide or AIBN, as free radical source, leading to the corresponding products in moderate yields (*Scheme 27*).[61] Recently, Ghorbani-Vaghei

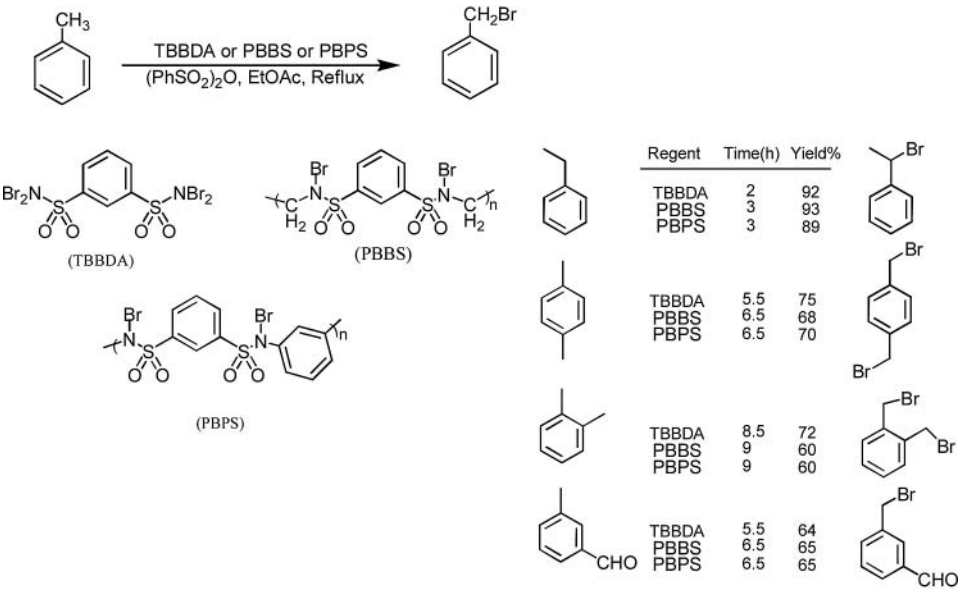


Scheme 27
Allylic and Benzylic Chlorination of Organic Compounds with NCSac

et al. reported a convenient method for the benzylic bromination of alkyl benzenes using *N,N,N′,N′*-tetrabromobenzene-1,3-disulfonamide [TBBDA], poly(*N,N′*-dibromo-*N*-ethylbenzene-1,3-disulfonamide) [PBBS], and novel reagent poly(*N,N′*-dibromo-*N*-phenyl-benzene-1,3-disulfonamide) [PBPS] in the presence of benzoyl peroxide and EtOAc (*Scheme 28*).[62]

3. Synthesis of α-Halocarbonyl Compounds

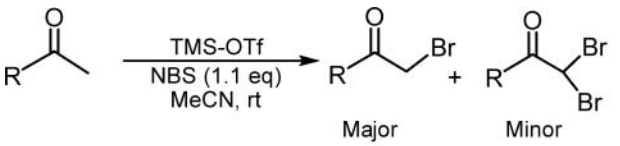
α-Haloketones are important intermediates in organic synthesis. They are conveniently converted to a number of important compounds. For example, they are transformed into (i) aldols stereospecifically in the presence of Cr(II) salts,[63] (ii) α-allylcarbonyl compounds by reaction with allylgallium/indium reagents,[64] (iii) arylacetic acids through Ag-assisted rearrangement of the primary or secondary α-bromo-alkylarylketones,[65] and (iv) β-diketones using $EtZnCH_2I$.[66] They are exploited in the conversion of vinylsilanes to ketones,[5] C-allylation of α,β-unsaturated amides,[67] etc.



Scheme 28
Benzylic Brominations using TBBDA or PBBS or PBPS

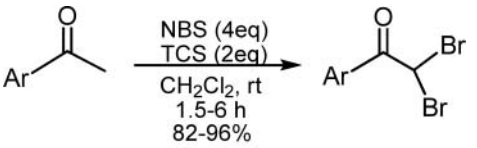
Treatment of variety of ketones and α,β-diketones with NBS in the presence of various catalysts produced the corresponding brominated ketones and diketones. With the trimethyl silyltrifluoromethanesulfonate (TMS-OTf) as catalyst, bromination of ketones with NBS lead to the monobrominated compounds as the major products and the dibrominated derivatives as by-products (*Scheme 29*).[68]

When arylketones were subjected to bromination using NBS in the presence of tetrachlorosilane (TCS), dibrominated products are obtained at the sole products (*Scheme 30*).[69]



R	Time (h)	Yield (%)
4-MeO–Ph	24	89:7
4-Cl–Ph	24	90:4
2-Naphthyl	24	62:1
t-Butyl	24	88:12

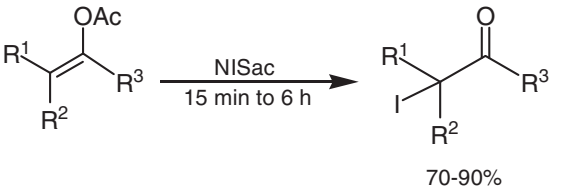
Scheme 29
Synthesis of α-Bromoketones using NBS



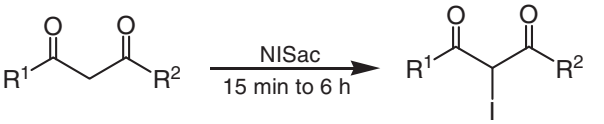
Ar = Ph, 4-MeO-Ph, 4-Cl-Ph, etc.

Scheme 30
Synthesis of α-Dibromoketones using NBS

Dolenc reported the iodination of enol acetates and 1,3-diones with *N*-iodosaccharin to the corresponding α-iodoketones and 2-iodo-1,3-diones at room temperature under mild conditions in good yields and short reaction times (*Scheme 31*).[70]



$R^{1,}$ R^2 , R^3 = Alkyl or Aryl



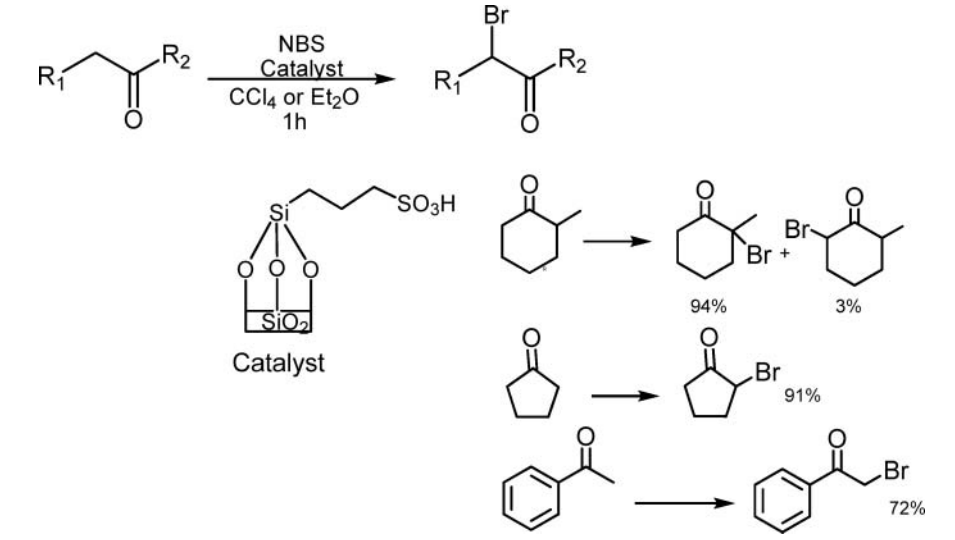
$R^{1,}$ R^2 , R^3 = Alkyl or Aryl

Scheme 31
Iodination of Enol Acetates and 1,3-Diones with NISac

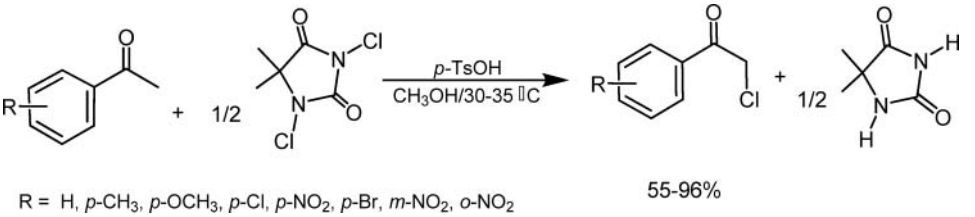
A wide range of carbonyl compounds were selectively transformed into the corresponding α-monobrominated products by treatment with NBS in the presence of sulfonic acid functionalized silica as a catalyst (*Scheme 32*).[71]

1,3-Dichloro-5,5-dimethylhydantoin (DCH) was used for the α-monochlorination of acetophenone derivatives under mild conditions (*Scheme 33*).[72]

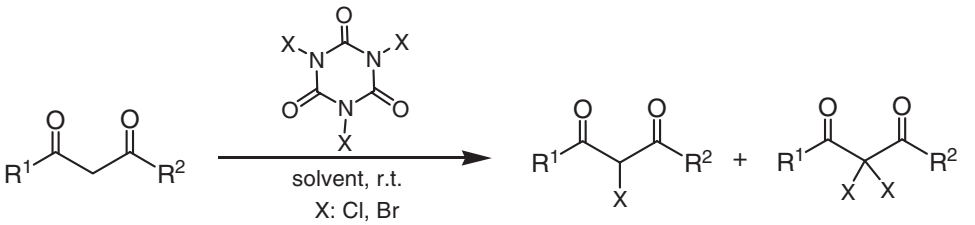
The reaction of β-dicarbonyl compounds (β-ketoesters and β-diketones) with 0.34 mol equiv of trichloro- and tribromoisocyanuric acids produced regioselectively the corresponding α-halo-β-dicarbonyl compound. On the other hand, utilization of 0.68 mol equiv of the trihaloisocyanuric acid produced the α,α-dihalo-β-dicarbonyl compound (*Scheme 34*).[73] The reaction conditions are safe and mild, and the quantity of halogen incorporated in the substrate is dependent on the ratio of trihaloisocyanuric acid/substrate.



Scheme 32
α-Monobromination of Carbonyl Compounds with NBS

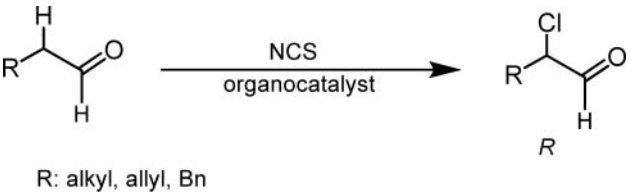


Scheme 33
α-Monochlorination of Acetophenones with DCH



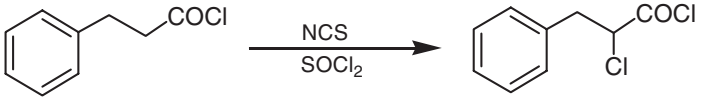
Scheme 34
Halogenation of β-Dicarbonyl Compounds with Trihaloisocyanuric Acid

The enantioselective α-chlorination of aldehydes by NCS catalyzed by L-proline amide and (*2R,5R*)-diphenylpyrrolidine was achieved (*Scheme 35*).[74,75] The aldehydes were isolated with excellent yield (up to 99%) and optical purity (up to 95%).



Scheme 35
Enantioselective α-Chlorination of Aldehydes by NCS Catalyzed by L-Proline Amide

An efficient and chemoselective α-chlorination of acyl chloride was accomplished with NCS in thionyl chloride as a solvent in the presence of catalytic amount of hydrochloric acid (*Scheme 36*).[76,77] The rate of this ionic reaction was retarded when α-substituents were present.



Scheme 36
α-Chlorination of Acyl Chloride with NCS

II. Application of *N*-Halo Compounds in Protection and Deprotection Chemistry

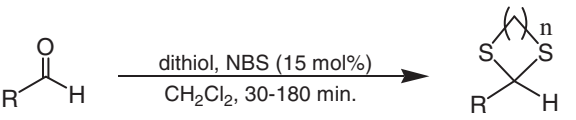
The protection and deprotection of functional groups play a crucial role in organic synthesis, especially in multi-step syntheses involving more than one functionality where chemoselectivity is required.[78] Several other reagents with their advantages and limitations are described in the literature, but *N*-halo reagents have been used as useful and effective catalysts for this purpose.

1. Protection and Deprotection of Carbonyl Groups

The protection of carbonyl functionality as a dithioacetal[78] is important in the total synthesis of complex natural and non-natural products.[79] Thioacetals are quit stable toward a wide variety of reagents and are also useful in organic synthesis as acyl carbanion equivalents in C-C bond-forming reaction.[80]

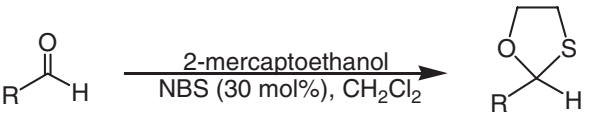
Kamal *et al*. described a mild and highly chemoselective procedure for the effective conversion of aldehydes in presence of ketones (added as a separate compound) into 1,3-dithiolanes and 1,3-dithianes using catalytic amount of *N*-bromosuccinimide (NBS) under neutral reaction conditions (*Scheme 37*).[81]

The role of NBS is not clear but a plausible explanation is that NBS react, first with the dithiol to generate HBr, which may activate the carbonyl group for further reaction with dithiol to generate corresponding product. The same authors also reported an efficient oxathioacetalization, thioacetalization and transthioacetalization of carbonyl compounds in high yields employing NBS as a catalyst (*Scheme 38*).[82]



R: aryl, alkyl, alkenyl n: 2, 3

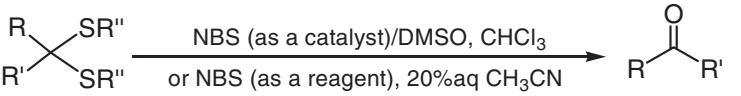
Scheme 37
Thioacetalization of Aldehydes using NBS



R: aryl, alkyl, alkenyl

Scheme 38
Oxathioacetalization of Carbonyl Compounds by NBS

N-Bromosuccinimide has been described as a deprotection agent or catalyst for the regeneration of a wide range of carbonyl compounds (*Scheme 39*).[83,84]



R, R', R'': H, Alkyl or Aryl

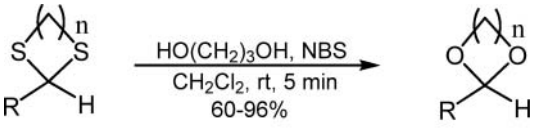
Scheme 39
Regeneration of Carbonyl Compounds by NBS

N-Bromosuccinimide (NBS) or *N*-chlorosuccinimide (NCS) were successfully used for interconversion of a range of 1,3-oxathiolanes, 1,3-dithiolanes and 1,3-dithianes to their acetals at ambient temperature (*Scheme 40*).[85]

N,N′-Diiodo-*N,N′*-ethanediylbis(4-methylbenzene)sulfonamide has been used for the deprotection of aliphatic and aromatic 1,3-dithianes to their corresponding carbonyl compounds under mild condition (*Scheme 41*).[86]

The deprotection of 1,3-oxathiolanes has been carried out with [BNBTS] in good yields under mild conditions (*Scheme 42*).[87]

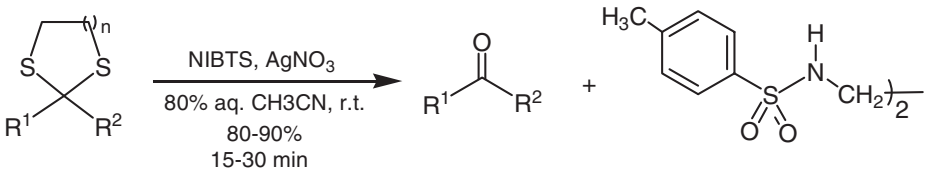
Recently, a simple and efficient deprotection of 1,3-dithianes and 1,3-dithiolanes of aromatic, aliphatic and α,β-unsaturated aldehydes and ketones to the corresponding parent carbonyl compounds under solvent-free conditions using poly(*N,N′*-dibromo-*N*-ethyl-benzene-1,3-disulfonamide) [PBBS], *N,N,N′,N′*-tetrabromobenzene-1,3-disulfonamide [TBBDA] and NBS at room temperature was reported (*Scheme 43*).[88]



n: 2, 3

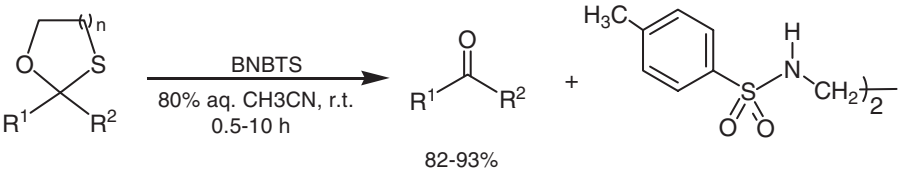
R = alkyl, aryl

Scheme 40
Interconversion of a Range of 1,3-Dithiolanes and 1,3-Dithianes to their Acetals by NBS

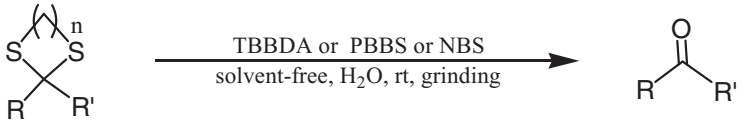


R^1, R^2 = Alkyl, Ary, H
n = 1, 2

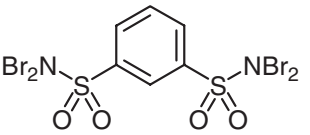
Scheme 41
Deprotection of 1,3-Dithianes by NIBTS



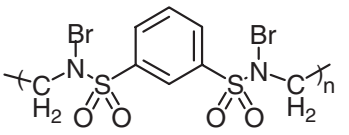
Scheme 42
Deprotection of 1,3-Oxathiolanes by BNBTS



n: 2, 3
R: aryl, alkyl
R': alkyl, H



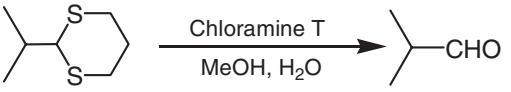
(TBBDA)



(PBBS)

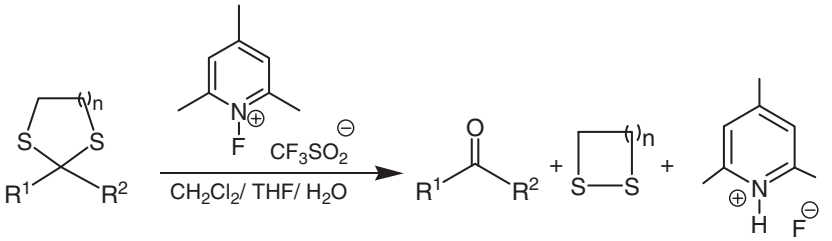
Scheme 43
Deprotection of 1,3-Dithianes and 1,3-Dithiolane by TBBDA or PBBS or NBS

Chloroamine T reacts with a variety of 1,3-dioxathiolanes, 1,3-dithiolanes and cleaves them to the original carbonyl compounds (*Scheme 44*).[89]



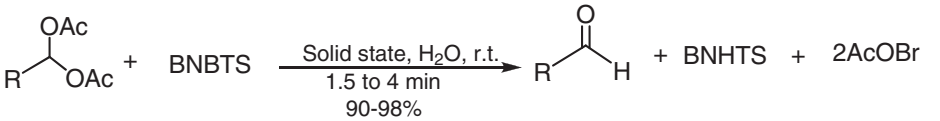
Scheme 44
Deprotection of 1,3-Dithiolane by Chloramine-T

N-Fluoro-2,4,6-trimethylpyridinium triflate efficiently cleaves dithioacetals to the parent carbonyl compounds (*Scheme 45*).[90]



Scheme 45
Deprotection of 1,3-Dithiolane with *N*-Fluoro 2,4,6-trimethylpyridinium Triflate

Conversion of 1,1-diacetates to aldehydes has been described using [BNBTS] in high yields and short time at room temperature under solvent-free condition (*Scheme 46*).[91]

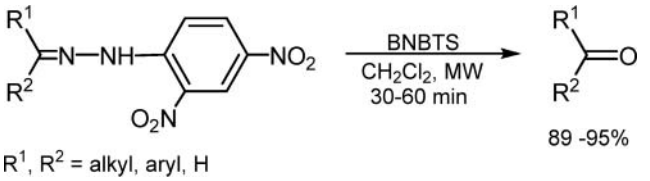


m-$NO_2C_6H_4$	3 min	94%
p-$NO_2C_6H_4$	4.5 min	92%
$PhCH{=}CH_2$	4 min	96%

Scheme 46
Conversion of 1,1-Diacetate to Aldehyde by BNBTS

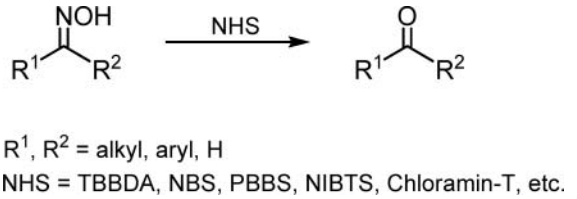
The deprotection of 2,4-dinitrophenylhydrazones to the corresponding carbonyl compounds has been reported in good yields with [BNBTS] under microwave irradiation (*Scheme 47*).[92]

The protection of carbonyl compounds is very important in multi-step synthesis. Protected carbonyl compounds such as oximes, semicarbazones, phenylhydrazone derivates, diacetal, dithianes, etc. are easily prepared and are highly stable compounds used extensively for the protection, purification and characterization of carbonyl compounds. *N*-Halo compounds are good reagents to accomplish these goals and have been used widely.



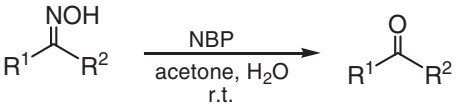
Scheme 47
Deprotection of 2,4-Dinitrophenylhydrazones by BNBTS

Recently a broad range of *N*-halosulfonamides (NHSs) has been reported for the regeneration of carbonyl compounds from oximes (*Scheme 48*).[93–100]



Scheme 48
Deprotection of Oximes to Carbonyl Compounds by NHS

NBP has been found to be an efficient and selective reagent for the mild oxidative cleavage of oximes to yield the corresponding carbonyl compounds in good to excellent yields (*Scheme 49*).[101]

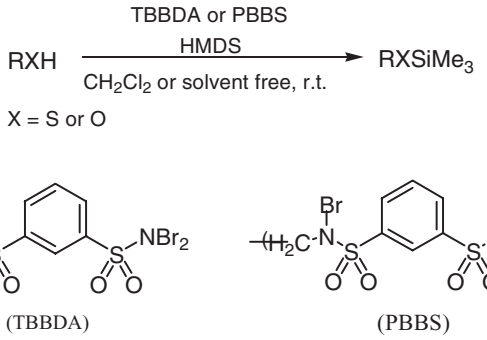


Scheme 49
Cleavage of Oximes to Carbonyl Compounds by NBP

2. Protection and Deprotection of Amines, Thiols and Hydroxy Groups

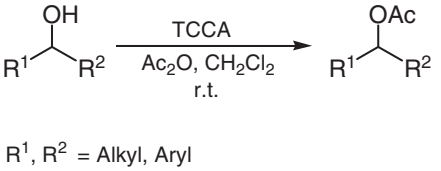
The protection of the *OH*, *NH* and *SH* groups is an important process in multi-step synthesis. One of the popular methods for this purpose is to transform the hydroxy group into the corresponding silyl ether. Ghorbani-Vaghei *et al*. have described a protocol for the mild and rapid silylation of alcohols, phenols, and thiols using hexamethyldisalazane (HMDS) in the presence of poly(*N*-bromobenzene-1,3-disulfonamides) [PBBS] and *N,N,N′,N′*-tetrabromobenzene-1,3-disulfonamide [TBBDA] as efficient catalysts under various conditions (*Scheme 50*).[102]

The protection of alcohols, amines, and thiols using acid anhydrides has been extensively used by organic chemists for nearly one century.[103] For this purpose, catalysts have



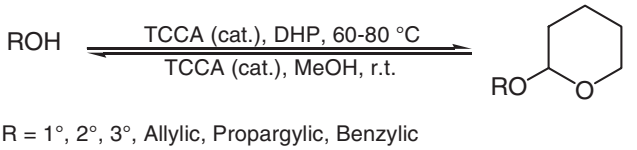
Scheme 50
Silylation of Alcohols, Phenols, and Thiols

been used for the rapid and efficient acylation of alcohols, phenols, amines and thiols. Acylation of primary, secondary and tertiary alcohols was achieved by the reaction with acetic anhydride and TCCA at room temperature in good to excellent yields (*Scheme 51*).[104]



Scheme 51
Acylation of Alcohols by TCCA

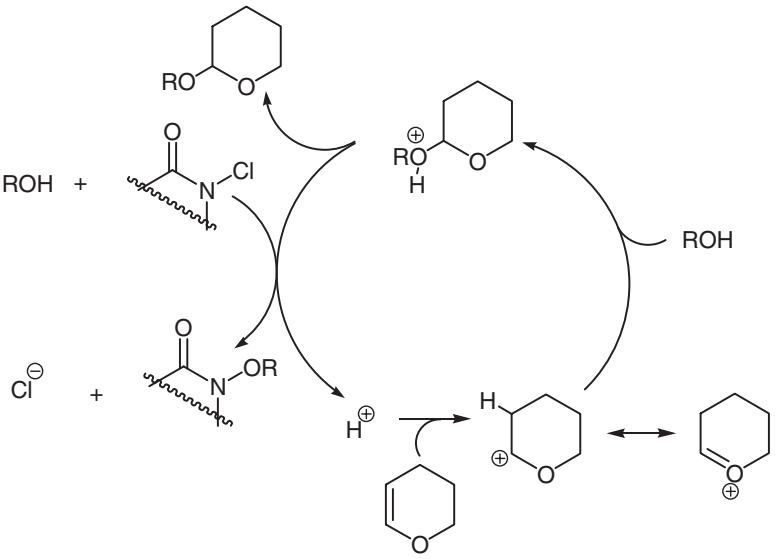
An easy and general method for the deprotection of thioacetals to the corresponding carbonyl compounds uses TCCA/silica gel in the presence of water.[105] Similar reactions were also carried out in non-aqueous conditions ($CHCl_3$ and DMSO) at room temperature.[106] The same group took advantage of TCCA in the catalytic preparation and cleavage of THP-ethers of various hydroxy groups in high yields (*Scheme 52*).[107]



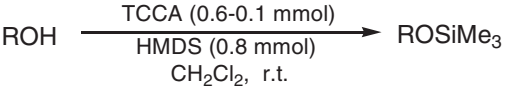
Scheme 52
Synthesis of THP-Ethers by TCCA

A mechanism was proposed for these transformations (*Scheme 53*).

A novel and efficient trimethylsilylation of various alcohols and phenols was efficiently carried out with hexamethyldisilazane (HMDS) in the presence of catalytic amounts of TCCA in good to excellent yields in dichloromethane at room temperature (*Scheme 54*).[108]



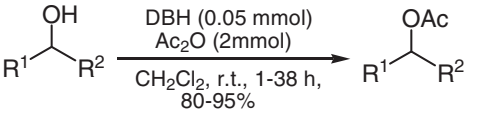
Scheme 53
Proposed Mechanism



R = 1°, 2°, 3°, Benzylic, Naphtyl

Scheme 54
Trimethylsilylation of Alcohols with HMDS and TCCA

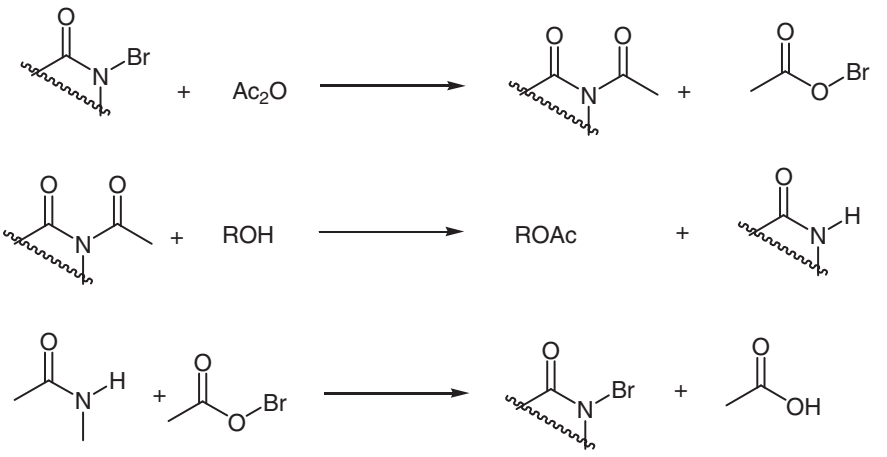
Recently, an efficient and high yielding method for the acylation of alcohols with acetic anhydride using DBH has been reported (*Scheme 55*).[104] The proposed mechanism, which was based on activation of Ac_2O by the *in situ* generated H^+, is shown in *Scheme 56*.



$R^1 = R^2$ = Alkyl or Aryl

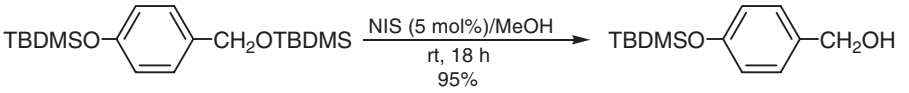
Scheme 55
Acylation of Alcohols with Acetic Anhydride using DBH

t-Butyldimethylsilyl (TBDMS) ethers were easily deprotected in excellent yields by treatment with a catalytic amount of *N*-iodosuccinimide (NIS) in methanol. This method is



Scheme 56
Proposed Mechanism for Acylation

able to deprotect TBDMS ethers of alcohols in the presence of TBDMS ethers of phenols (*Scheme 57*).[109]



Scheme 57
Deprotection of TBDMS Ethers in the Presence of TBDMS with NIS

III. *N*-Halo Compounds as Oxidizing Agents

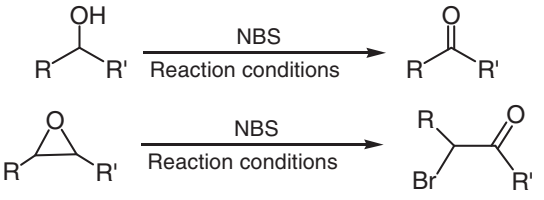
Another important application of *N*-halo reagents in organic chemistry is the oxidation of different functional groups through the release of halonium ions.

1. Oxidation of Alcohols to Carbonyl Compounds

The oxidation of the hydroxy group to carbonyl functionality is an important transformation in organic synthesis and several methods are available to accomplish this conversion under a variety of reaction conditions.[110–113] Because of its significant role in synthetic chemistry, this reaction continues to receive attention from chemists in search of newer and selective oxidation protocols.[114]

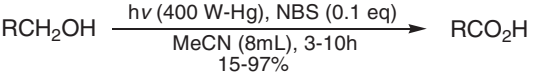
Oxidation of a variety of alcohols and epoxides has been carried out using NBS in the presence of different catalysts in good to excellent yields (*Scheme 58*).[115,116]

Itoh and Kuwabara have suggested a practical procedure for the oxidation of primary alcohols to the corresponding carboxylic acids. A wide range of alcohols have been oxidized into carboxylic acid, in the presence of a catalytic amount of NBS in oxygen atmosphere under *hν* irradiation (*Scheme 59*).[117]



R, R' = Alkyl or Aryl
Reaction conditions: [$NH_4Cl/CH_3CN/H_2O$ (7:3)
or [Co(II) acetylacetonate/CH_3CN, reflux

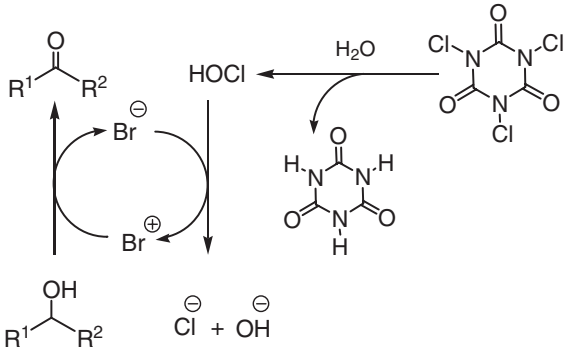
Scheme 58
Oxidation of Variety of Alcohols using NBS



R = Alkyl or Aryl

Scheme 59
Oxidation of Alcohols to Carboxylic Acids using NBS

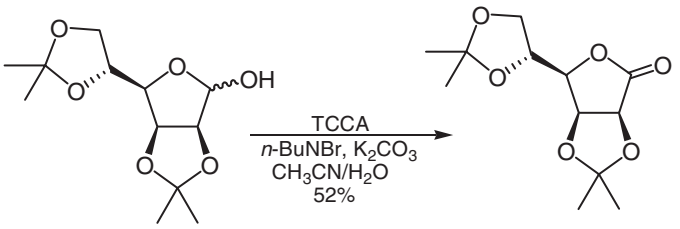
TCCA catalyzes in dehydrogenation of primary and secondary alcohols to aldehydes and ketones, respectively. Chemoselective oxidation of benzylic and secondary alcohols was achieved by the use of TCCA and wet SiO_2 in the presence of a catalytic amount of KBr under heterogeneous conditions at room temperature (*Scheme 60*).[118]



Scheme 60
Oxidation of Alcohols to Carbonyl Compounds using TCCA

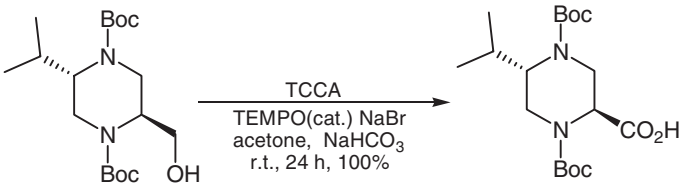
In some cases TCCA has been used for the oxidation of primary alcohols to carboxylic acids. For instance, the combined use of catalytic $RuCl_3$ (1.0 mol%) and stochiometric amount of TCCA in the presence of *n*-Bu_4NBr and K_2CO_3, led to the smooth oxidation of primary alcohols to carboxylic acids.[119] Secondary alcohols were oxidized to ketones using

a similar set of reagents. The method is mild and permits the chemoselective oxidation of alcohols in the presence of other sensitive functional groups (*e. g*. alkene) (*Scheme 61*).



Scheme 61
Oxidation of Secondary Alcohols to Ketones using TCCA in the Presence of *n*-Bu_4NBr

Efficient oxidation of primary alcohols to the corresponding carboxylic acids was carried out at room temperature in acetone/water, using TCCA in the presence of a catalytic amount of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy).[120] The mild conditions of procedure and the total absence of any transition metal make the reaction suitable for safe laboratory use (Scheme 62). A mechanism was proposed for these reactions (*Scheme 63*).

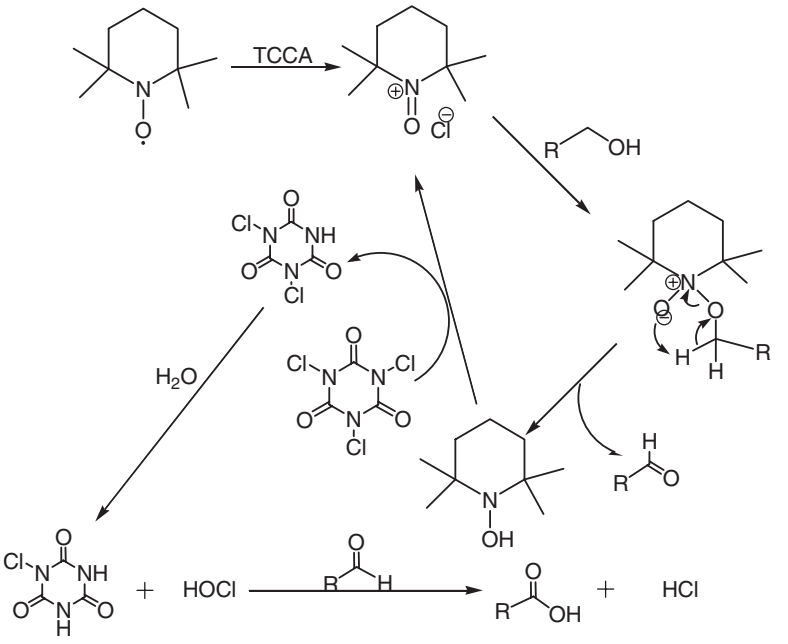


Scheme 62
Oxidation of Alcohols to Carboxylic Acids using NBS in the Presence TEMPO

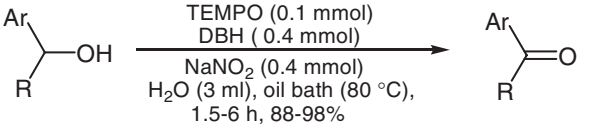
DBH in the presence of $NaNO_2$ was used as a co-catalyst for the acceleration of the aerobic oxidation of benzylic alcohols in water catalyzed by TEMPO (*Scheme 64*). All reactions were performed at 80 °C and the products were obtained in good to high yields.[121]

Primary alcohols are chemoselectively oxidized by NCS to aldehydes in the presence of TEMPO catalyst. A broad range of aliphatic, benzylic and allylic alcohols were oxidized, without any over oxidation (*Scheme 65*).[122]

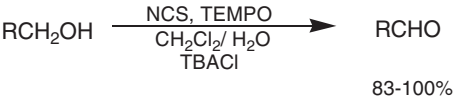
Ghorbani-Vaghei and Veisi reported an efficient and mild methodology for the oxidation of primary and secondary alcohols to the corresponding carbonyl functions with *N,N,N′,N′*-tetrabromobenzene-1,3-disulfonamide and poly(*N*-bromobenzene-1,3-disulfonamide) using microwave irradiation under solvent-free conditions. Aliphatic, benzylic and allylic alcohols are rapidly oxidized to aldehydes without over-oxidation to carboxylic acids. Secondary carbinols are slowly oxidized so that the reaction is highly chemoselective (*Scheme 66*).[123]



Scheme 63
Proposed Mechanism of Oxidation with TCCA



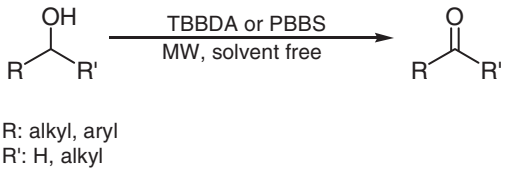
Scheme 64
Oxidation of Alcohols to Carbonyl Compounds using DBH and TEMPO

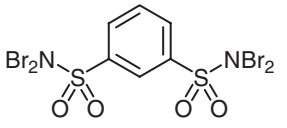


Scheme 65
Chemoselective Oxidation of Alcohols to Aldehydes by NCS

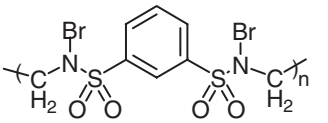
2. Oxidation of Thiols into Disulfides

N-Bromosaccharin has successfully been used for the chemoselective oxidation of thiols to their corresponding disulfides in dichloromethane under microwave irradiation conditions in high yields (*Scheme 67*).[124] Two reasonable mechanisms, an ionic path and a radical path, were suggested for this conversion.



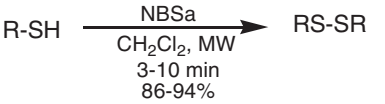


(TBBDA)

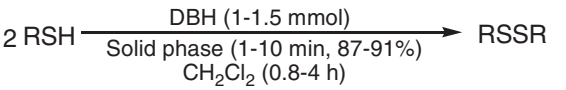


(PBBS)

Scheme 66
Oxidation of Alcohols to Carbonyl Compounds using TBBDA or PBBS in MW



Scheme 67
Oxidation of Thiols to the Corresponding Disulfides by NBSa

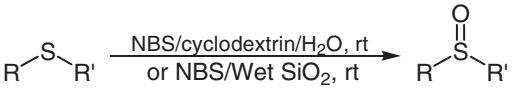


Scheme 68
Oxidation of Thiols to the Corresponding Disulfides by DBH

Khazaei *et al.* described a simple method for the oxidation of thiols to disulfides (*Scheme 68*). A solution of DBH and the thiol in dichloromethane gave the corresponding disulfide in excellent yields.[125]

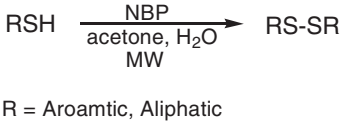
A good range of sulfoxides have been prepared *via* oxidation of sulfides using NBS in the presence of hydrated silica gel or β–cyclodextrin/water in reasonable yields (Scheme 69).[126,127]

NBP was used for the facile oxidation of thiols to symmetrical disulfides in a mixture of acetone-water under microwave irradiation. Both aromatic and aliphatic thiols were



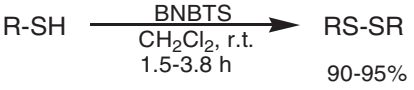
Scheme 69
Oxidation of Thiols to Sulfones by NBS

selectively oxidized to disulfides (sulfoxides, sulfones, sulfonic acid were not formed) in good to excellent yields (*Scheme 70*).[128]



Scheme 70
Oxidation of Thiols to Disulfides by NBP

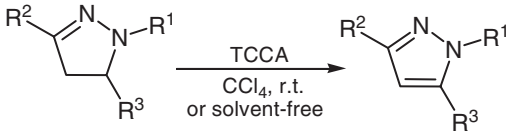
Efficient oxidative coupling of thiols by BNBTS has led to the production of the corresponding disulfides at room temperature in good to excellent yields (*Scheme 71*).[129]



Scheme 71
Oxidation of Thiols to Their Corresponding Disulfides by BNBTS

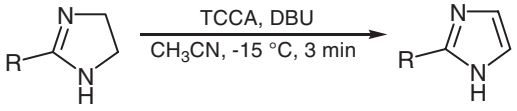
3. Aromatization of Various Cyclic Compounds

N-Halo reagents have also been applied to the aromatization of cyclic compounds. TCCA was used for the oxidation of 1,3,5-trisubstituted-2-pyrazolines to the corresponding pyrazoles under either heterogeneous or solvent-free conditions in good yields at room temperature (*Scheme 72*).[130]



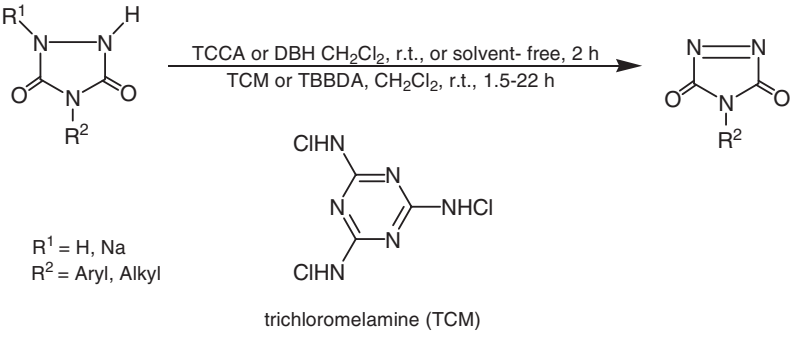
Scheme 72
Oxidation of 1,3,5-Trisubstituted-2-pyrazolines by TCCA

Similar reactions were carried out under microwave irradiation in acetic acid.[131] Dehydrogenation of a variety 2-imidazolines to the corresponding imidazoles was achieved by TCCA in the presence of DBU (*Scheme 73*).[132] Chemoselective oxidation of these compounds was successfully carried out in the presence of sulfides and alcohols.



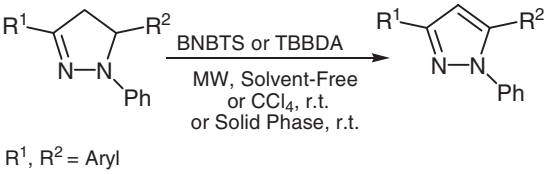
Scheme 73
Oxidation of 2-Imidazolines to Imidazoles by TCCA

TCCA, DBH, TBBDA and TCM were used as effective oxidizing agents for the conversion of urazoles and *bis*-urazoles to the triazolinediones under both heterogeneous and also solvent-free conditions with excellent yields at room temperature (*Scheme 74*).[133–135]



Scheme 74
Oxidation of Urazoles to Triazolinediones

N,N,N′,N′-Tetrabromobenzene-1,3-disulfunamide (TBBDA), BNBTS and PBBS were used as efficient reagents for the oxidation of 1,3,5-trisubstituted-2-pyrazolines to the corresponding pyrazoles in solvent-free conditions under microwave irradiation or room temperature (*Scheme 75*).[136–139]

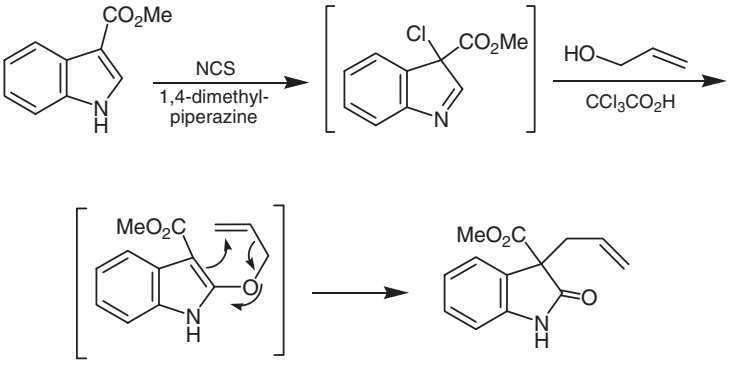


Scheme 75
Oxidation of 2-Imidazolines to Imidazoles by TBBDA, BNBTS and PBBS

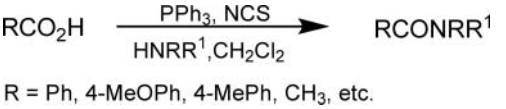
IV. *N*-Halo Compounds in Rearrangements and Functional Group Transformations

N-Halo reagents can be used to mediate several types of rearrangements and functional group transformations. Thus, the treatment of 3-indolecarboxylate with NCS and different primary and secondary alkenols afforded 3-allylated 2-indolones in good yields (*Scheme 76*).[140] This novel transformation involves α-chlorination, addition of alcohol to the imine bond, and [3,3]-sigmatropic rearrangement of the intermediate. This Claisen rearrangement is highly stereoselective for *Z*-alkenols. With *E*-alkenols the reaction gave the products as mixtures of diastereomers presumably due to an unfavorable steric interaction of the methyl ester with the *E* substituent forcing the adoption of a boat-like transition state.

Aromatic and aliphatic acids were converted in excellent yields into amides in the presence of NCS and triphenyphosphine (*Scheme 77*). The reaction was conducted under



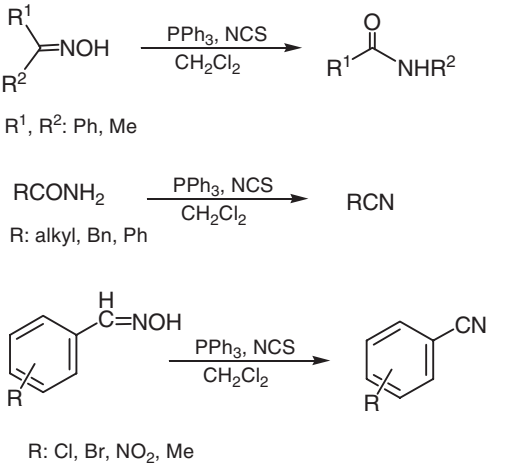
Scheme 76
Treatment of 3-Indolecarboxylate with NCS



Scheme 77
Conversion of Acids into Amides with NCS and PPh_3

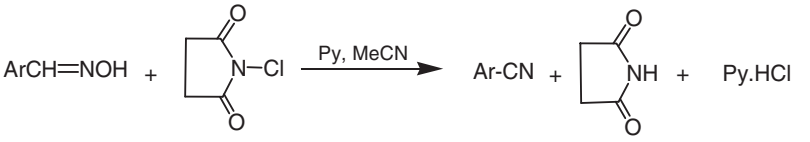
mild conditions and with a wide variety of substrates, including the sensitive and sterically congested abietic acid and primary as well as secondary amines.[141]

The Beckmann rearrangement of ketoximes with a mixture of triphenyphosphine and NCS in dichloromethane at room temperature afforded secondary amides, whereas primary amides and aldoximes were rapidly converted into the corresponding nitriles (*Scheme 78*).[142]



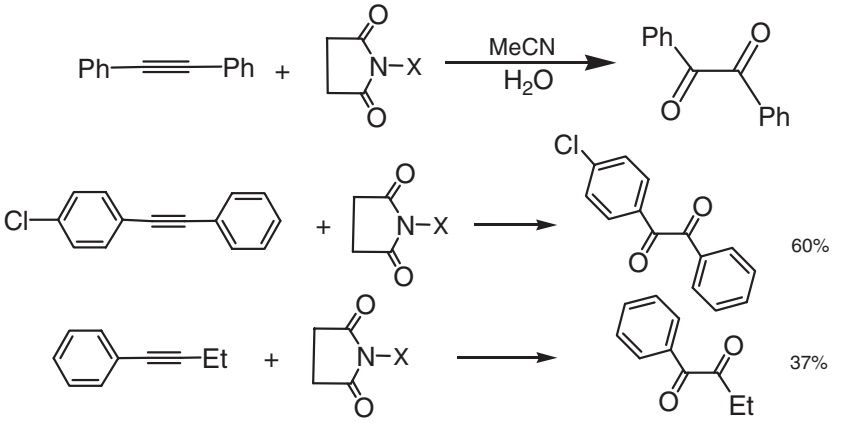
Scheme 78
Beckmann Rearrangement of Ketoximes with NCS and PPh_3

Benzaldoximes substituted with electron-donating groups are dehydrated to the corresponding benzonitriles by *N*-chlorosuccinimide/pyridine in acetonitrile (*Scheme 79*).[143] Benzaldoxime itself and alkanal oximes afford the corresponding aldehydes.



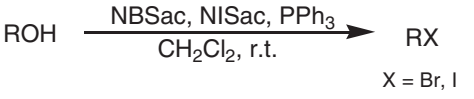
Scheme 79
Conversion of Benzaldoximes into Benzonitriles with NCS

A convenient and practical approach to α-diketones *via* reactions of alkynes with *N*-iodosuccinimides/water at 70 °C has been developed by Fu *et al*. (*Scheme 80*).[144]



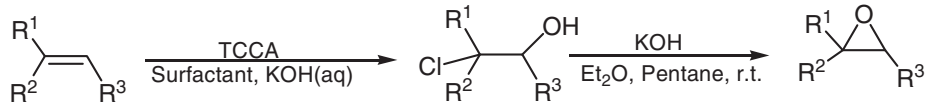
Scheme 80
Conversion of Acetylenes to α-Diketones with *N*-Halosuccinimides

The conversion of alcohols into the corresponding bromides and iodides is an important transformation in organic synthesis. *N*-Bromo- and *N*-iodosaccharin in combination with Ph_3P are highly reactive reagents for the conversion of aliphatic hydroxy compounds (primary and secondary) into the corresponding bromides and iodides using dichloromethane as solvent at room temperature under neutral conditions (*Scheme 81*).[145]



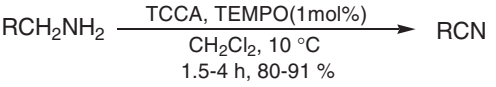
Scheme 81
Conversion of Alcohols into the Corresponding Bromides and Iodides

The preparation of epoxides was efficiently achieved by the reaction of alkenes with TCCA in aqueous acetone followed by treatment of the resulting chlorohydrin with aqueous KOH in ether/pentane (*Scheme 82*).[146]



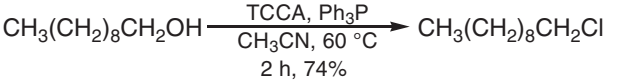
Scheme 82
Preparation of Epoxides from Alkenes in the Presence TCCA

Chen and co-workers reported the oxidation of primary amines into nitriles by TCCA in the presence of a catalytic amount of TEMPO under mild conditions (*Scheme 83*).[147] Optimization of the reaction conditions showed that the best results were obtained in dichloromethane at 10 °C and the use of 1 mol% of the catalyst.



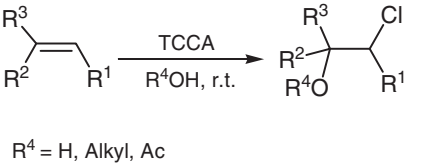
Scheme 83
Oxidation of Primary Amines into Nitriles by TCCA and TEMPO

Hiegel *et al.* reported a procedure for the conversion of alcohols (1° and 2°) to alkyl chlorides using TCCA in the presence of triphenylphosphine (*Scheme 84*).[148]



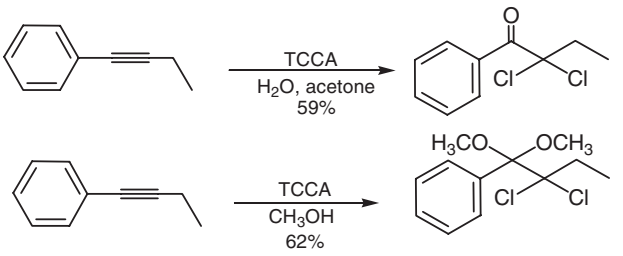
Scheme 84
Conversion of Alcohols to Alkyl Chlorides using TCCA

The preparation of various β-chloroethers, β-chloroacetates and chlorohydrins was achieved by the reaction of alkenes with TCCA in alcohols (MeOH, EtOH, *i*-PrOH and *t*-BuOH) and acetic acid, respectively (*Scheme 85*).[149]



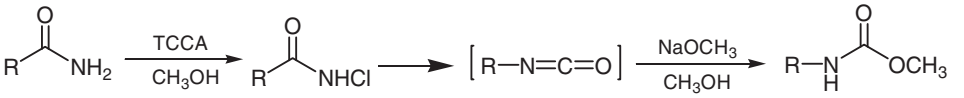
Scheme 85
Preparation of Diverse β-Chloroethers by the Reaction of Alkenes with TCCA in Alcohols

Alkynes were reacted with TCCA in the presence of water in acetone or acetonitrile to form α,α-dichloro ketones and in methanol to form α,α-dichlorodimethyl ketals (*Scheme 86*).[150]



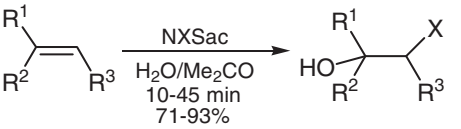
Scheme 86
Reaction of Alkynes with TCCA in the Presence of Water and Methanol

Amides were chlorinated on nitrogen using TCCA and the intermediate *N*-chloroamides then rearranged to the corresponding methyl carbamates by sodium methoxide in methanol *via* the corresponding isocyanates (*Scheme 87*).[151]



Scheme 87
TCCA in Rearrangements of Amides

The reactions of NCSac and NBSac with alkenes (cyclohexene, styrene, α-methylstyrene, and 1-hexene) gave the corresponding halohydrins in H_2O and acetone as solvent (*Scheme 88*).[32]



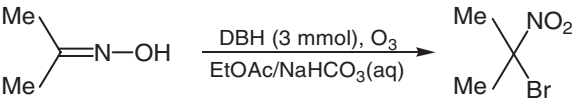
X = Cl or Br
R^1 = *n*-Bu, Ph
R^2 = H
R^3 = H, Me

Scheme 88
Reaction of NBSac with Alkynes in the Presence of H_2O

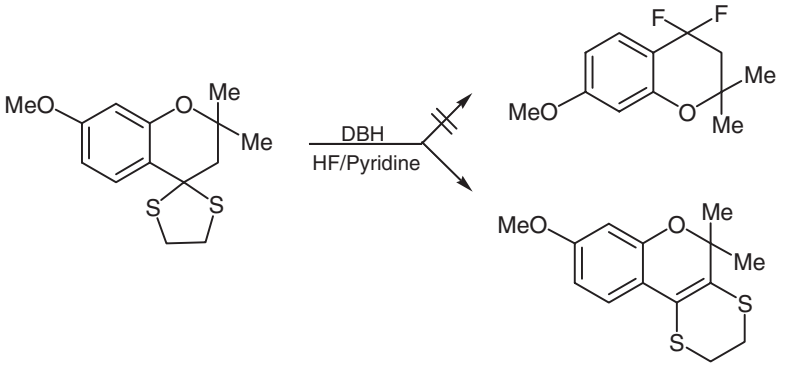
Walters *et al.* studied the use of DBH for the oxidation of oximes to *gem*-halonitro compounds in the presence of ozone (*Scheme 89*).[152] The bromo derivatives were obtained in 44–73% yields.

When 1,3-dithiolanes bearing a phenyl or substituted aromatic group and a methyl (or methylene) group attached to C-2 were treated with DBH in the presence of HF/pyridine, a rearrangement took place instead of *gem*-difluorination (*Scheme 90*).[153]

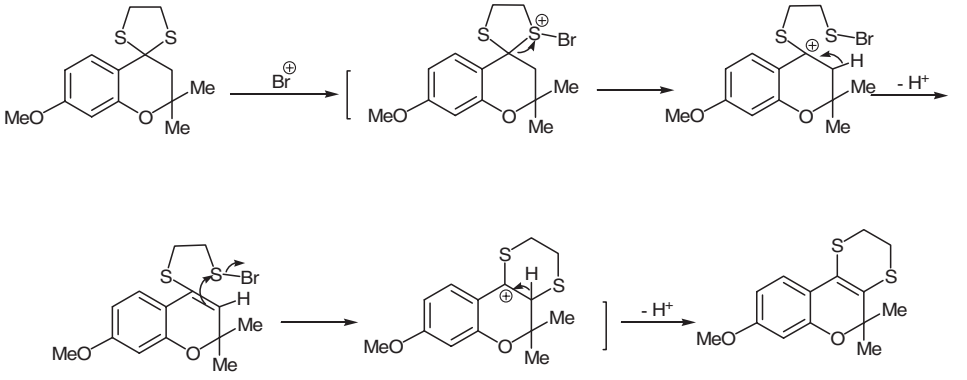
A mechanism proposed for this rearrangement is shown in *Scheme 91*.



Scheme 89
Conversion of Oximes to *gem*-Halonitro Compounds by DBH



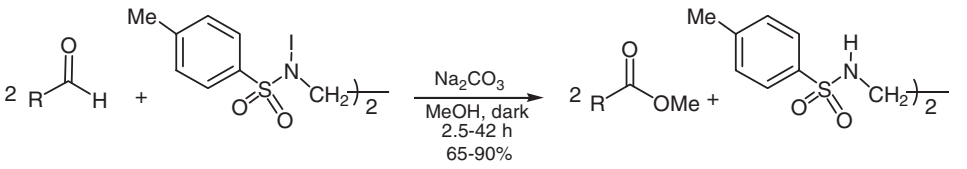
Scheme 90
Rearrangement of 1,3-Dithiolanes in the presence of DBH



Scheme 91
Proposed Mechanism

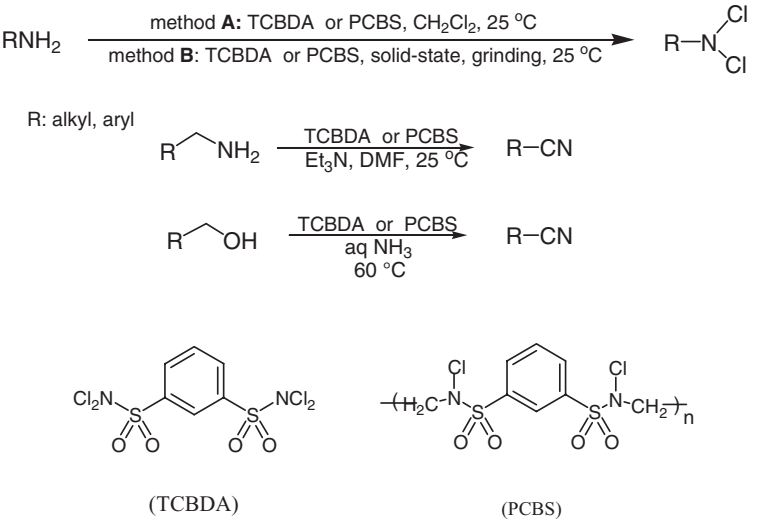
N,N′-Diiodo-*N,N′*-1,2-ethanediyl*bis*(*p*-toluenesulfonamide) (NIBTS) has converted aldehydes to methyl esters in the presence of methanol in good yields at room temperature (*Scheme 92*).[154]

Ghorbani-Vaghei and Veisi have reported poly(*N,N′*-dichloro-*N*-ethyl-benzene-1,3-disulfonamide) [PCBS] and *N,N,N′,N′*-tetrachlorobenzene-1,3-disulfonamide [TCBDA] as novel reagents for the preparation of *N*, *N*-dichloroamines from corresponding amines, and nitriles from primary amines under various conditions. Furthermore, a simple and effective



Scheme 92
Conversion of Aldehydes to Methyl Esters in Methanol and NIBTS

procedure for the direct oxidative conversion of alcohols to nitriles was successfully carried out with TCBDA and PCBS in aqueous ammonia (*Scheme 93*).[155]



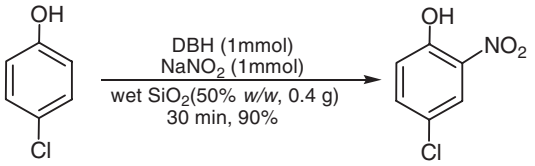
Scheme 93
TCBDA and PCBS as Novel Reagents for Preparation of *N*,*N*-Dichloroamines, Nitriles and Aldehydes

V. Catalytic Activity of *N*-Halo Compounds and Formation of Heterocyclic Compounds

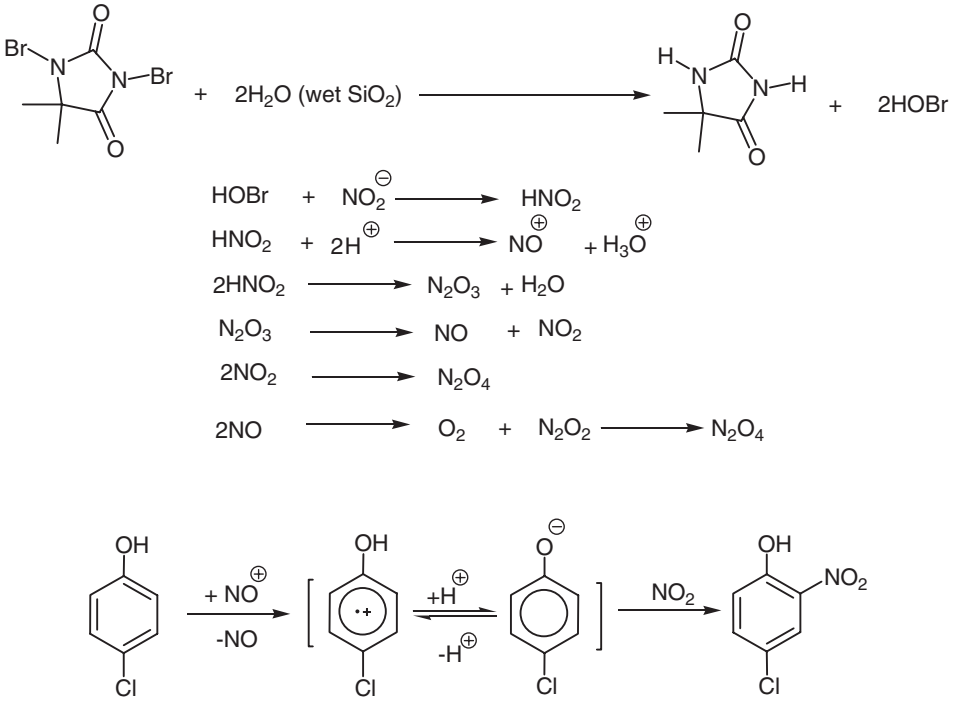
Since *N*-halo reagents contain halogen atom which are attached to nitrogen atoms, it is likely that they release X^+ *in situ* which can act as Lewis acid catalyst in the reaction medium. Recently was reported that DBH/$NaNO_2$/wet SiO_2 can be used as an efficient reagent system for the direct nitration of phenols (*Scheme 94*).[156] All reactions were performed at room temperature and under completely heterogeneous reaction conditions in moderate to good yields.

Since the reaction did not proceed in the absence of wet SiO_2, the following mechanism was proposed (*Scheme 95*).

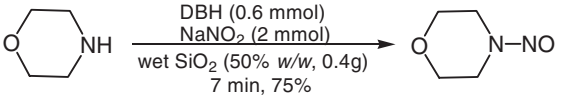
In the same manner, when *N*,*N*-dialkylamines are treated with DBH/$NaNO_2$/ wet SiO_2 reagent system, the corresponding *N*-nitroso derivatives are obtained in good to excellent yields (*Scheme 96*). The reaction conditions are very mild and completely heterogeneous.[157]



Scheme 94
Nitration of Phenols DBH/$NaNO_2$/wet SiO_2

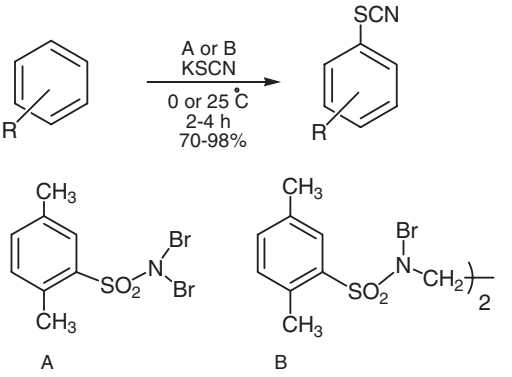


Scheme 95
Proposed Mechanism for Nitration



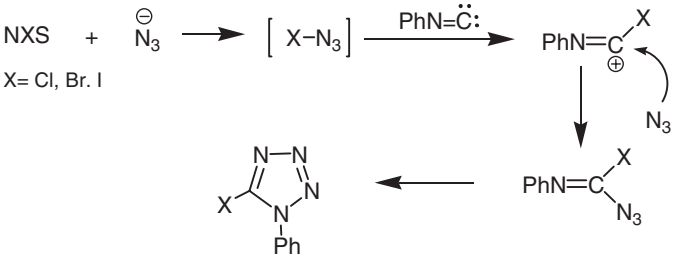
Scheme 96
N-Nitrosation of amines

N-Bromosulfonamides react with several types of aromatic compounds in the presence of KSCN at 0 or 25°C to afford arylthiocyanates (*Scheme 97*).[158]



Scheme 97
Synthesis of Arylthiocyanates by KSCN in Presence of *N*-Bromosulfonamides

N-Halosuccinimides have been used to facilitate new synthesis of heterocyclic systems. The treatment of phenyl isocyanide with NXS and sodium azide under phase-transfer catalysis conditions afforded 5-halo-1-phenyltetrazoles in good yields (*Scheme 98*). The active species is probably the halogen azide which add to phenyl isocyanide.[159]



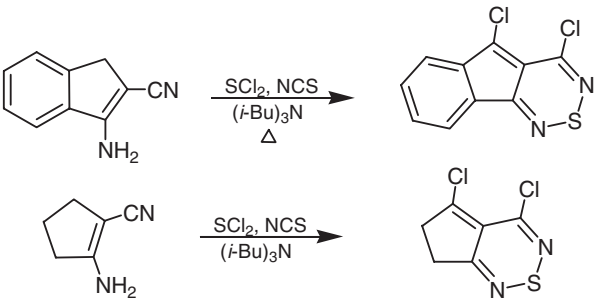
Scheme 98
Synthesis of 5-Halo-1-phenyltetrazoles from of Phenyl Isocyanide and NXS

3-Amino-1*H*-indene-2-carbonitrile reacted with sulfur dichloride in *tris*-(isobutyl)amine and NCS to give the corresponding indeno[1,2,6]thiadiazine in a reaction that involved dehydrogenation and chlorination of the cyclopentathiazine moiety (*Scheme 99*).[160]

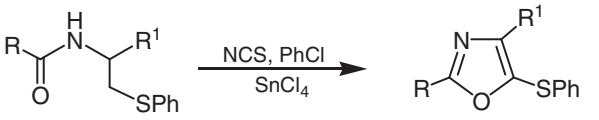
The application of the Pummerer reaction methodology to N-acylamino-2-thiophenyl derivatives with NCS and tin(IV) chloride provided a direct synthesis of 5-thiophenyl oxazoles (*Scheme 100*).[161]

NBS has been reported as a mild, efficient and natural catalyst for the preparation of dihydropyrimidinones under microwave irradiation (*Scheme 101*).[162]

Aziridine, an important three-memberd heterocyclic ring system, is a useful precursor for the synthesis of several biologically important compounds such as amino acids, amino



Scheme 99
Synthesis of Indeno[1,2,6]thiadiazine



R=aryl, heteroaryl, alkyl 50-77%

R^1=phenyl, alkyl, H

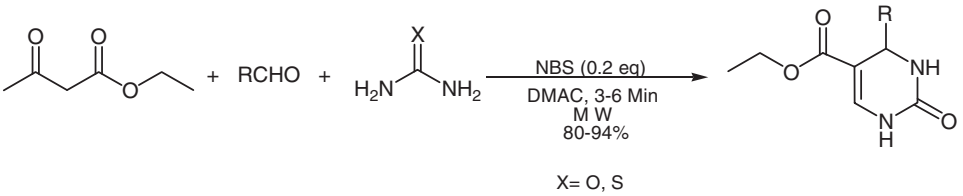
Scheme 100
Reaction of Triphenylformazanes with NCS and Formation of 2,3,5-Triphenylterazolium halides

sugars and alkaloids. For this purpose, chloramine-T has been used in the presence of various catalysts (*Scheme 102*).[163–169]

Although mechanistic aspects of the aziridation are not yet clear, Sudalai and co-workers have suggested an interesting mechanism for aziridation by NBS as catalyst (*Scheme 103*).[164]

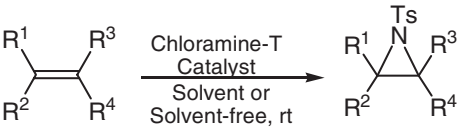
N-Chlorosaccharin has been shown to undergo electrophilic-Ritter type reaction with alkenes in acetonitrile; two different products have been obtained (imidazoline or aziridine). These reactions have been carried out at −42°C up to room temperature (*Scheme 104*).[170]

TCCA was used in the presence of base as an efficient oxidant for the epoxidation of enones and tandem oxidation-epoxidation of allylic alcohols in aqueous suspension system in the presence of a surfactant (*Scheme 105*).[146]



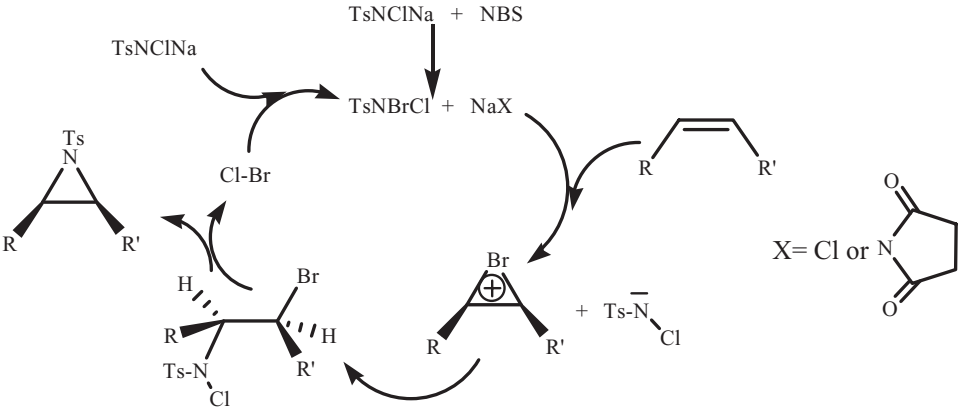
X= O, S

Scheme 101
Preparation of Dihydropyrimidinones Catalyzed by NBS

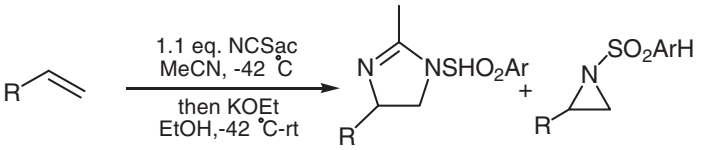


R^1, R^2, R^3 or R^4= Alkyl or Aryl
Solvent: CH_3CN or H_2O
Catalyst:HPA/CTAB/MS 5A, Py/HBr_3, I_2/BTEAC, CuI/Ptc, MPHT or NBS
Ts: $CH_3C_6H_4SO_2$

Scheme 102
Preparation of Aziridine Catalyzed by Chloramine-T



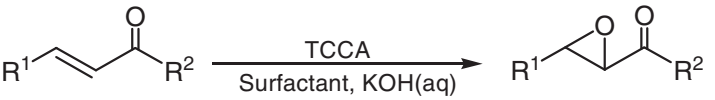
Scheme 103
Proposed Mechanism for Aziridation by NBS as Catalyst



Ar= 2-$EtO_2CC_6H_4$-
R= Aryl derivatives

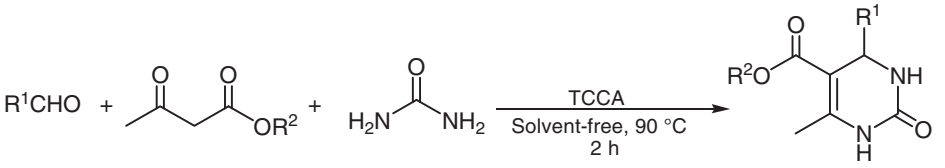
entry	R	imidazoline (%)	aziridine (%)
1	Ph	60	7
2	2-ClC_6H_4-	44	0
3	4-ClC_6H_4-	46	9
4	2-BrC_6H_4-	35	0
5	4-FC_6H_4-	45	13
6	3-MeC_6H_4-	47	10
7	4-MeC_6H_4-	24	23
8	2,4,6-triMeC_6H_4-	0	49
9	4-$MeOC_6H_4$-	0	0

Scheme 104
Electrophilic-Ritter Type Reaction with Alkenes



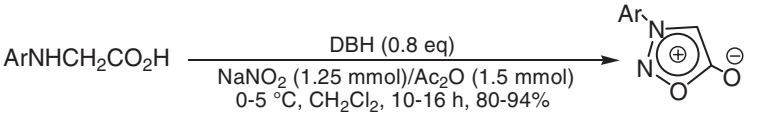
Scheme 105
Epoxidation of Enones in Presence of TCCA

TCCA was used efficiently for the synthesis of 3,4-dihydropyridine-2(1*H*)-ones through the three-component Biginelli reaction of a β-ketoester, an aldehyde and urea (*Scheme 106*).[171]



Scheme 106
Synthesis of 3,4-Dihydropyridine-2(1*H*)-ones in Presence of TCCA

In 2006, Azarifar *et al*. reported an efficient method for the conversion of various *N*-arylglycines to sydnones using 1,3-dibromo-5,5-dimethylhydantoin in the presence of $NaNO_2$/ Ac_2O under mild and neutral conditions (*Scheme 107*).[30]

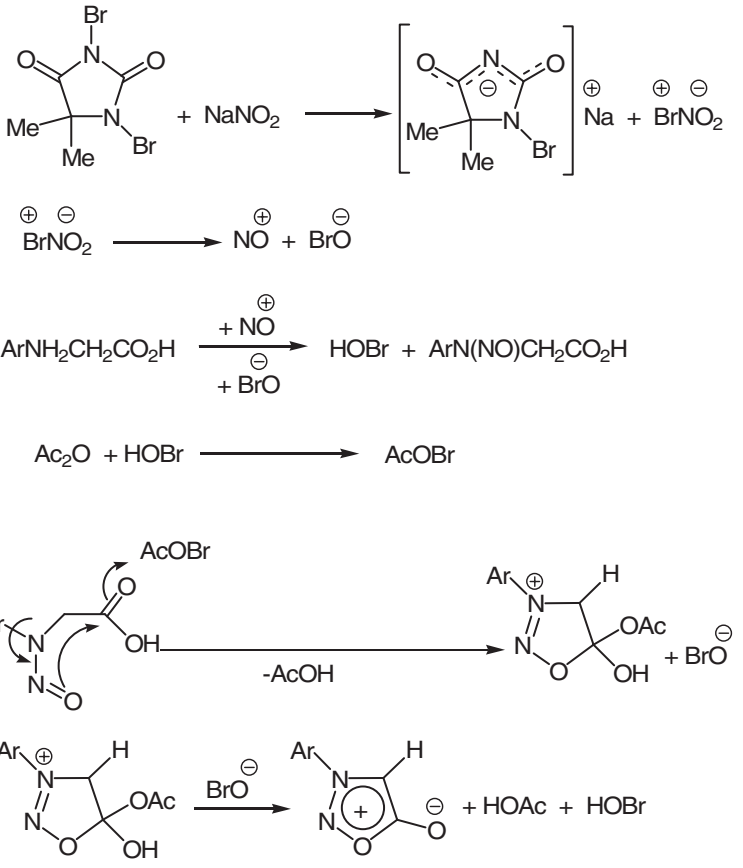


Scheme 107
Synthesis of Sydnones using 1,3-Dibromo-5,5-dimethylhydantoin

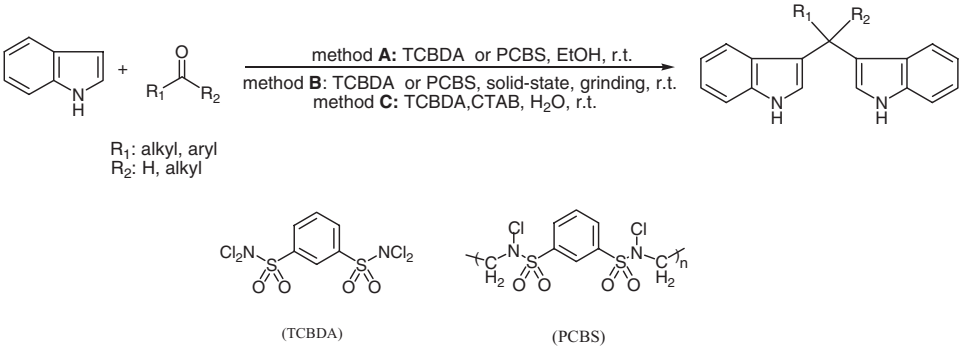
The following mechanism was proposed for these transformations (*Scheme 108*).

Ghorbani-Vaghei and Veisi introduced the novel catalytic reagents poly(*N*,*N*′-dichloro-*N*-ethylbenzene-1,3-disulfonamide) [PCBS] and *N,N,N′,N′*-tetrachlorobenzene-1,3-disulfonamide [TCBDA] for the efficient preparation of *bis*-indolyl, *tris*-indolyl, di(*bis*-indolyl), tri(*bis*-indolyl) and tetra(*bis*-indolyl) methanes from indole with various aldehydes and ketones in ethanol, water and under solid-state conditions at room temperature with excellent yields. This method is applicable to a wide range of aldehydes, including aromatic, aliphatic, α,β-unsaturated, heterocyclic substrates, and ketones. In addition, efficiency, mild reaction conditions, easy work-up, simplicity and chemoselectivity of this protocol provide a rapid, green, and low-cost procedure for the synthesis of these compounds (*Scheme 109*).[172]

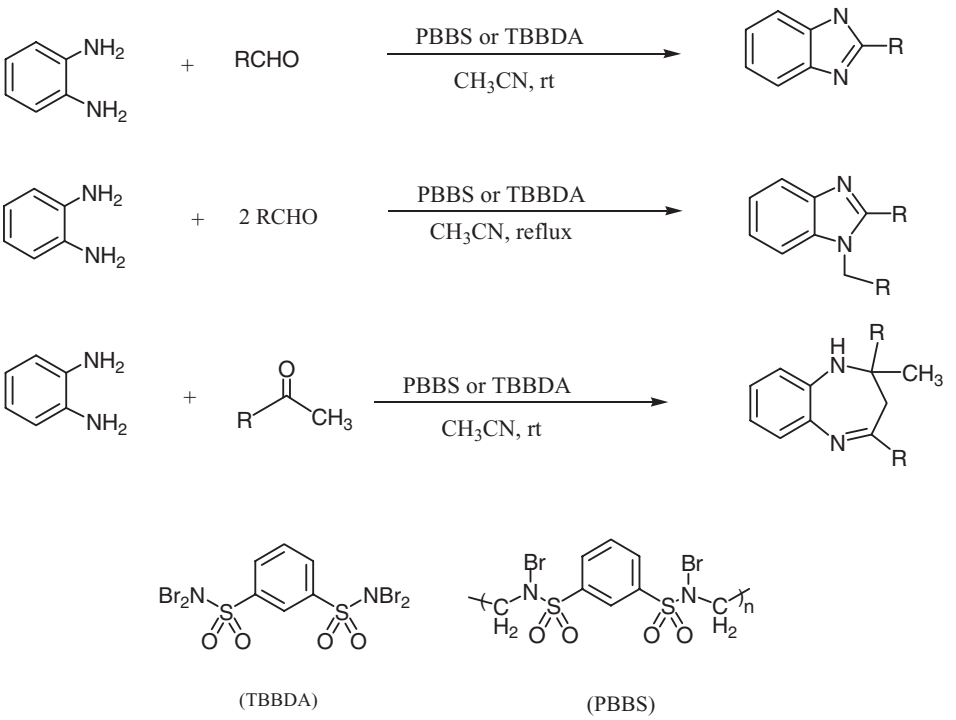
TBBDA and PBBS were found to be mild and effective catalysts for the synthesis of 2-aryl-1-arylmethyl-1H-1,3-benzimidazoles and 1,5-benzodiazepines and new reagents for the synthesis of 2-arylbenzimidazoles under mild conditions by the rapid condensation of



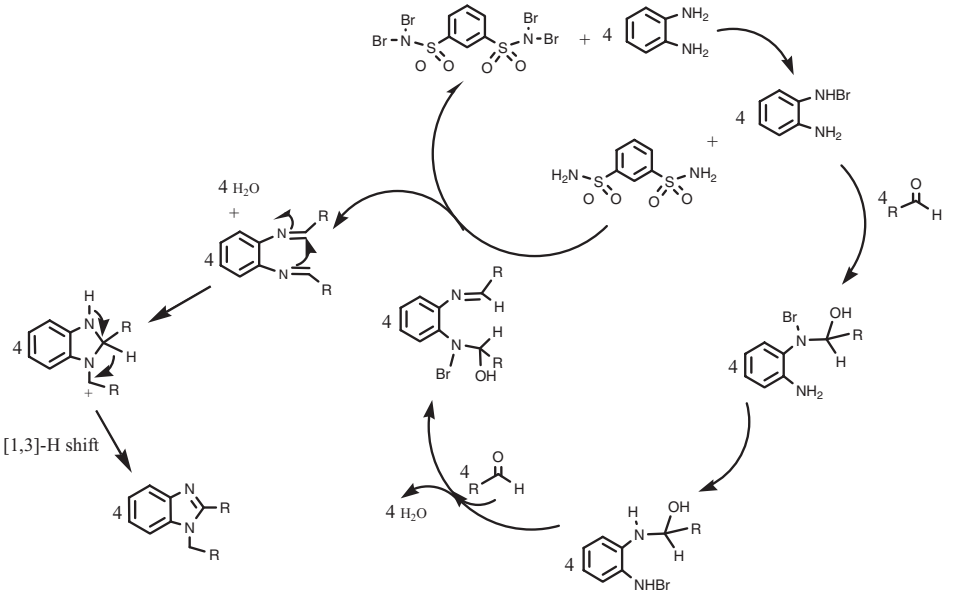
Scheme 108
Proposed Mechanism for Synthesis of Sydnones



Scheme 109
Preparation of *bis*-Indolyl, *tris*-Indolyl, Di(*bis*-indolyl), tri(*bis*-indolyl) and tetra(*bis*-indolyl)methanes Catalyzed by TCBDA or PCBS



Scheme 110
Synthesis of Benzimidazoles and 1,5-Benzodiazepines Catalyzed by TBBDA and PBBS

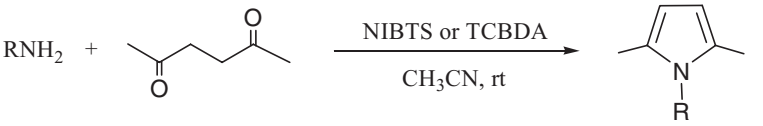


Scheme 111
Possible Mechanism for the formation of 2-Aryl-1-arylmethyl-1H-1,3-benzimidazoles

various aryl aldehyde and ketones with *o*-phenylenediamine (OPDA). Moreover, the method has advantages in terms of product yields, selectivity, operational simplicity (easy work-up of reactions) and environmental friendliness (non-corrosive reagent) (*Scheme 110*).[173]

The proposed mechanism for synthesis of the 1,2-disubstituted benzimidazoles may involve the iminium-catalyzed formation of *N,N′*-dibenzylidene-*o*-phenylenediamine, bromination, and ring closure to give a five-membered ring either in a sequential or a concerted manner (*Scheme 111*).

Futhermore, the same authors introduced the novel catalytic reagent *N,N,N′,N′*-tetrachlorobenzene-1,3-disulfonamide (TCBDA) and new catalytic reagents *N,N′*-diiodo-*N,N′*-1,2-ethandiyl *bis*(*p*-toluenesulfonamide) (NIBTS) for the synthesis of various substituted pyrroles by the Pall-Knorr reaction (*Scheme 112*).[174]



R: alkyl and aryl

Scheme 112
Synthesis of various Pyrroles by the Pall-Knorr Reaction

VI. Conclusions

It should be noted that a correct and updated citation and literature survey is very important for researchers to find relevant information, to pioneer new ideas, and to determine the progress of any subject. On the other hand, the published data using *N*-halo reagents indicate a wide synthetic potential of these reagents and a great interest of researchers in these compounds. A wide range of original procedures for the synthesis of various classes of organic compounds, including organic functional group transformations have been developed on the basis of the *N*-halo reagents. We believe that the present review article enhances information on this very important subject and will stimulate researchers active in this field to synthesize new *N*-halo reagents and to explore their applications in organic reactions and discover more and more applications of the existing *N*-halo reagents in organic synthesis.

Acknowledgements

We are thankful to Bu-Ali Sina University and Payame Noor University (PNU) for financial support. The authors thank their coworkers named in the references, for their experimental and intellectual contributions.

References

1. I. V. Koval, *Russ. J. Org. Chem.*, **38**, 327 (2002).
2. I. V. Koval, *Russ. J. Org. Chem.*, **37**, 297 (2001).

3. R. E. Banks, *J. Fluorine Chem.*, **87**, 1 (1998).
4. K. Kanie, M. Kuroboshi and T. Hiyama, *Nippon Kagaku Kaishi*, **11**, 749 (2000).
5. T. Umemoto, S. Fukami, G. Tomizawa, K. Harasawa, K. Kawada and K. Tomita, *J. Am. Chem. Soc.*, **112**, 8563 (1990).
6. G. R. Dake, M. D. B. Fenster, P. B. Hurley and B. O. Patrick, *J. Org. Chem.*, **69**, 5668 (2004).
7. X. L. Armesto, M. Canle, M. V. Garcia and J. A. Santaballa, *Chem. Soc. Rev.*, **27**, 453 (1998).
8. D. Cahard, C. Audouard, J. -C. Plaquevent and N. Roques, *Org. Lett.*, **2**, 3699 (2000).
9. E. Kolvari, A. Ghorbani-Choghamarani, P. Salehi, F. Shirini and M. A. Zolfigol, *J. Iran. Chem. Soc.*, **4**, 126 (2007); *Chem. Abstr.*, **147**, 142765 (2007).
10. L. Florvall, S. O. Ogren, *J. Med. Chem.*, **25**, 1280 (1982).
11. S. O. Ogren, H. Hall, C. Kohler, O. Magnusson, L. O. Lindbom, K. Angeby and L. Florvall, *Eur. J. Pharmocol.*, **102**, 459 (1984).
12. E. Yue, W. J. M. Gerdes and C. A. Mathis, *J. Org. Chem.*, **56**, 5451 (1991).
13. A. I. Meyers, J. R. Flisk and R. A. Aitken, *J. Am. Chem. Soc.*, **109**, 5446 (1987).
14. J. Y. Merour, J. Y. Coadou and F. Tatibouet, *Tetrahedron Lett.*, 1053 (1982).
15. G. A. Olah, S. J. Kuhn and B. A. Hardie, *J. Am. Chem. Soc.*, **86**, 1055 (1964).
16. A. R. Leed, S. D. Boettger and B. Ganem, *J. Org. Chem.*, **45**, 1098 (1980).
17. Y. Zhang, K. Shibatomi and H. Yamamoto, *Synlett*, 2837 (**2005**).
18. N. B. Barhate, A. S. Gajare, R. D. Wakharkar and A. V. Bedekar, *Tetrahedron Lett.*, **39**, 6349 (1998).
19. J. Dakka and Y. Sassa, *J. Chem. Soc.*, 1421 (**1987**).
20. H. Lubbecke and P. Boldt, *Tetrahedron*, **34**, 1577 (1978).
21. K. S. Webb and D. Levy, *Tetrahedron Lett.*, **36**, 5117 (1995).
22. R. Ghorbani-Vaghei and H. Jalili, *Synthesis*, 1099 (**2005**).
23. R. Ghobani-Vaghei, *Tetrahedron Lett.*, **44**, 7529 (2003).
24. A. Khazaei and A. Shirdarreh, *Synth. Commun.*, **29**, 4079 (1999).
25. J. Auerbach, S. A. Weissman, T. J. Blacklock, M. R. Angeles and K. Hoogsteen, *Tetrahedron Lett.*, **34**, 931 (1993).
26. C. Chassaing, A. Hauderchy and Y. Langlois, *Tetrahedron Lett.*, **38**, 4415 (1997).
27. H. Eguchi, H. Kawaguchi, S. Yoshinnaga, A. Nishida, T. Nishiguchi and S. Fujisaki, *Bull. Chem. Soc. Jpn*, **67**, 1918 (1994).
28. A. Alam, Y. Takaguchi, H. Ito, T. Yushida and S. Tsuboi, *Tetrahedron*, **61**, 1909 (**2005**).
29. A. Alam, Y. Takaguchi and S. Tsuboi, *J. Fac. Environ. Sci. Technol. Okayama University*, **10**, 105 (2005); *Chem. Abstr.*, **147**, 230574p (2005).
30. D. Azarifar and H. Ghasemnezhad-Bosra, *Synthesis*, 1123 (**2006**).
31. K. Tanemura, T. Suzuki, Y. Nishida, K. Satsumabayashi and T. Horaguchi, *Chem. Lett.*, 932 (**2003**).

32. S. P. L. Souza, J. F. M. Silva and M. C. S. Mattos, *J. Braz. Chem. Soc.*, **14**, 832 (2003); *Chem. Abstr.*, **142**, 25745u (2003).

33. B. Zajac, *J. Org. Chem.*, **64**, 1902 (1999); *Chem. Abstr.*, **130**, 237351 (1999).

34. R. Rajagopal, S. A. Siddiqui, T. Daniel, R. J. Lahoti and K. V. Srinivasan, *J. Mol. Catal. A: Chemical*, **210**, 165 (2004).

35. M. Bagheri, N. Azizi and M. R. Saidi, *Can. J. Chem.*, **83**, 146 (2005).

36. A. Khazaei, A. Aminmanesh and V. R. Safi, *J. Chin. Chem. Soc.*, **52**, 559 (2005); *Chem. Abstr.*, **144**, 6539 (2005).

37. R. C. Larock, *Comprehensive Organic Transformations*, 1st ed.; VCH: Weiheim, 315, (1989).

38. R. S. Neale, R. G. Schepers and M. R. Walsh, *J. Org. Chem.*, **29**, 3390 (1964).

39. D. F. Paul and P. Haberfield, *J. Org. Chem*., **41**, 3170 (1976).

40. T. E. Nickson and C. A. Roche-Dolson, *Synthesis*, 669 (**1985**).

41. R. A. Day, J. A. Blake and C. E. Stephenes, *Synthesis*, 1586 (**2003**).

42. E. B. Merkushev, *Synthesis*, 923 (**1988**)

43. S. N. Georgiades and J. Clardy, *Org. Lett.*, **8**, 4251 (2006).

44. R. F. Heck, *Org. React.*, **27**, 345 (1982).

45. J. K. Stille, *Angew. Chem., Int. Ed. Engl.*, **25**, 508 (1986).

46. A. Suzuki and N. Miyaura, *Chem. Rev.*, **95**, 2457 (1995).

47. N. Fusetani and S. Matsunaga, *Chem. Rev.*, **93**, 1793 (1993).

48. P. Bovonsombat, J. Leykajarakul, C. Khan, K. Pla-on, M. M. Krause, P. Khanthapura, R. Ali and N. Doowa, *Tetrahedron Lett.*, **50**, 2664 (2009).

49. K. K. Laali, M. Tanaka, F. Forohar, M. Cheng and J. C. Fetzer, *J. Fluorine Chem.*, **91**, (1998).

50. R. E. Banks and A. Khazaei, *J. Fluorine Chem.*, **46**, 297 (1990).

51. R. E. Banks, M. K. Besheesh, S. N. Mohialdin-Khaffaf and I. Sharif, *J. Fluorine Chem.*, **81**, 157 (1997).

52. R. E. Banks, M. K. Besheesh, W. Fraenk and T. M. Klapotke, *J. Fluorine Chem.*, **124**, 229 (2003).

53. M. Zupan, J. Iskra and S. Stavber, *Tetrahedron*, **52**, 11341 (1996).

54. K. Ziegler, A. Späth, E. Schoof, W. Schuman and E. Winkelman, *Justus Liebigs Ann. Chem.*, **551**, 80 (1942).

55. E. I. Sanchez and M. J. Fomarola, *Synthesis*, 736 (**1976**).

56. S. Kotha, S. Halder and K. Lahiri, *Synthesis*, 339 (**2002**).

57. J. Clayden, C. McCarthy, N. Westlund and C. S. Frampton, *J. Chem. Soc., Perkin Trans. 1*, 1363 (**2000**).

58. E. I. Sanchez and M. J. Furamola, *J. Org. Chem.*, **47**, 1588 (1982).

59. A. Khazaei, R. Ghorbani-Vaghei and E. Karkhanei, *Synth. Commun.*, **32**, 2107 (2002).

60. D. Suarez, G. Laval, S. M. Tu, D. Jiang, C. L. Rabinson, R. Scott and B. T. Golding, *Synthesis*, 1807 (**2009**).

61. J. M. Bachhawat, A. K. Koul, B. Prashad, N. S. Ramegowda, C. K. Narang and N. K. Mathur, *Indian J. Chem.*, **11**, 609 (1973).

62. R. Ghorbani-Vaghei, M. Chegini, H. Veisi, and M. Karimi-Tabar, *Tetrahedron Lett.*, **50**, 1861 (2009).

63. J. -E. Dubois, G. Axiotis and E. Bertounesque, *Tetrahedron Lett.*, **26**, 4371 (1985).

64. K. Takami, S. -I. Usugi, H. Yorimitsu and K. Oshima, *Synthesis*, 824 (**2005**).

65. C. Giordano, G. Castaldi, F. Casagrande and L. Abis, *Tetrahedron Lett.*, **23**, 1385 (1982).

66. L. Li, P. Cai, D. Xu, Q. Guo and S. Xue, *J. Org. Chem.*, **72**, 8131 (2007).

67. J. Kondo, H. Shinokubo and K. Oshima, *Angew. Chem., Int. Ed.*, **42**, 825 (2003).

68. S. K. Guha, B. Wu, B. S. Kim, W. Baik and S. Koo, *Tetrahedron Lett.*, **47**, 291 (2006).

69. S. S. Elmorsy, D. S. Badawy and T. K. Khatab, *Phosphorus, Sulfur, and Silicon*, **181**, 2012 (2005).

70. D. Dolenc, *Synth. Commun.*, **33**, 2917 (2003).

71. B. Das, K. Venkateswalu, H. Holla and M. Krishnaiah, *J. Mol. Catal. A: Chemical*, **253**, 107 (2006).

72. Z. J. Xu, D. Y. Zhang and X. Z. Zou, *Synth. Commun.*, **36**, 255 (2006).

73. G. F. Mendonça, H. C. Sindra, L. S. de Almeida, P. M. Esteves and M. C. S. de Mattos, *Tetrahedron Lett.*, **50**, 473 (2009).

74. N. Halland, A. Braunton, S. Bachmann, M. Marigo and K. A. Jorgensen, *J. Am. Chem. Soc.*, **126**, 4790 (2004).

75. N. Halland, M. A. Lie, A. Klaresgaard, M. Marigo, B. Schiott and K. A. Jorgensen, *Chem. Eur. J.*, **11**, 7083 (2005).

76. D. N. Harpp, L. Q. Bao, C. J. Black, J. G. Gleason and J. G. Smith, *J. Org. Soc.*, **40**, 3420 (1975).

77. D. N. Harpp, L. Q. Bao, C. J. Black, J. G. Smith and J. G. Gleason, *Tetrahedron Lett.*, **15**, 3235 (1974).

78. T. W. Green and P. G. M. Wuts, *Protecting Groups in Organic Synthesis*, 3rd ed.; John Wiley& Sons: New York, 329 (1999).

79. T. W. Greene. *Protective Groups in Organic Synthesis*; John Wiley: New York, 129 (1981).

80. H. Yu, D. Dong, Y. Ouyang and Q. Liu. *Can. J. Chem.*, **83**, 1741 (2005).

81. A. Kamal and G. Chouhan, *Synlett*, 474 (**2002**).

82. A. Kamal, G. Chouhan and K. Ahmed, *Tetrahedron Lett.*, **43**, 6947 (2002).

83. N. Iranpoor, H. Firouzabadi and H. R. Shaterian, *Tetrahedron Lett.*, **44**, 4769 (2003).

84. H. R. Shaterian and H. Hadadzadeh, *Phosphorus, Sulfur, and Silicon*, **181**, 1071 (2006).

85. B. Karimi, H. Seradj and J. Maleki, *Tetrahedron*, **58**, 4513 (2002).

86. R. Ghorabni-Vaghei and M. A. Zolfigol, *J. Chin. Chem. Soc.*, **52**, 327 (2005); *Chem. Abstr.*, **144**, 12365p (2005).

87. R. Ghorbani-Vaghei and A. Khazaei, *Phosphorus, Sulfur and Silicon*, **179**, 1787 (2004); *Chem. Abstr.*, **142**, 56217u (2005).

88. R. Ghorbani-Vaghei and H. Veisi, *Arkivoc*, 44 (**2009**).

89. D. W. Emerson and H. Wynberg, *Tetrahedron Lett.*, 3445 (1971).

90. A. S. Kiselyov and L. Streowski, *Tetrahedron*, **49**, 2151 (1993).

91. R. Ghorbani-Vaghei, S. A. Akbari, M. A. Zolfigol, B. F. Mirjalili and A. Bamoniri, *Mendeleev Commun.*, 55 (**2006**).

92. A. Khazaei and R. Ghorbani-Vagei, *Molecules*, **7**, 465 (2002).

93. M. Tajbakhsh, A. Khazaei, M. Shabani-Mahalli and R. Ghorbani- Vaghei, *J. Chem. Res.* 141 (2004).

94. R. Ghorbani-Vaghei and A. Khazaei, *Phosphorus, Sulfur and Silicon*, **179**, 1169 (2004).

95. A. Khazaei, A. Aminimanesh and A. Rostami, *Phosphorus, Sulfur and Silicon*, **179**, 2483 (2004).

96. A. Khazaei, A. Aminimanesh and A. H. Ghasemi, *Synthesis*, 2784 (**2004**).

97. A. Khazaei, S. Mallakpour and R. Ghorbani- Vaghei, *Iran Polym. J.*, **12**, 115 (2003); *Chem. Abstr.*, **140**, 288041u (2004).

98. A. Khazaei and R. Ghorbani-Vaghei, *Tetrahedron Lett.*, **43**, 3073 (2002).

99. A. Khazaei, R. Ghorbani-Vaghei and M. Tajbakhsh, *Tetrahedron Lett.*, **42**, 5099 (2001)

100. A. Khazaei and A. Aminimanesh, *Synthesis*, 1739 (**2004**).

101. A. Khazaei, A. Amin Manesh and A. Rostami, *J. Chem. Res.*, 695 (**2004**).

102. R. Ghorbani-Vaghei, M. A. Zolfigol, M. Chegeny and H. Veisi, *Tetrahedron Lett.*, **47**, 4505 (2006).

103. A. Verley and F. Bolsing, *Ber. Dtsch. Chem. Ges.*, **34**, 3354 (1901).

104. M. A. Zolfigol, A. Khazaei, A. Ghorbani-Choghamarani and A. Rostami, M. Hajjami, *Catal. Commun.*, **7**, 399 (2006).

105. H. Firouzabadi, N. Iranpoor and H. Hazarlkhani, *Phosphorus, Sulfur*, **177**, 2571 (2002).

106. N. Iranpoor, H. Firouzabadi and H. R. Shaterian, *Tetrahedron Lett.*, **44**, 4769 (2003).

107. H. Firouzabadi, N. Iranpoor and H. Hazarkhani, *Synth. Commun.*, **34**, 3623 (2004).

108. A. Khazaei, M. A. Zolfigol, A. Rostami and A. G. Choghamarani, *Catal. Commun.*, **8**, 543 (2007).

109. B. Karimi, A. Zamani and D. Zareyee, *Tetrahedron Lett.*, **45**, 9139 (2004).

110. B. M. Trost, in *Comprehensive Organic Synthesis (Oxidation)*, S. V. Ley, Ed.; Pergamon: New York, 260 (1991).

111. J. Einhorn, C. Einhorn, F. Ratajczak and J. L. Pierre, *J. Org. Chem.*, **61**, 7452 (1996).

112. J. Muzrt, A. N. Ait Ajjou and S. Ait Mohand, *Tetrahedron Lett.*, **35**, 1989 (1994).

113. R. A. Lee and D. S. Donald, *Tetrahedron Lett.*, **38**, 3857 (1997).

114. I. E. Marko, P. R. Giles, M. S. Taukazaki and M. Brown, *J. Urch, Science.*, **274**, 2044 (1996); *Chem. Abstr.*, **126**, 103888 (1997).

115. S. L. Jain and B. Sain, *Synth. Commun.*, **36**, 1459 (2006).

116. N. S. Krishnaveni, K. Surendra and K. R. Rao, *Adv. Synth. Catal.*, **346**, 346 (2004).

117. K. Kuwabara and A. Itoh, *Synthesis*, 1949 (**2006**).

118. M. A. Zolfigol, F. Shirini and A. Ghorbani-Choghamarani, *Synthesis*, 2043 (**2006**).

119. H. Yamaoka, N. Moriya and M. Ikunaka, *Org. Proc. Res. Develop.*, **8**, 931 (2004).

120. L. Deluca and G. Giacomelli, *J. Org. Chem.*, **68**, 4999 (2003).

121. R. Liu, C. Dong, X. Liang, X. Wang and X. Hu, *J. Org. Chem.*, **70**, 729 (2005).

122. J. Eihorn, C. Eihorn, F. Ratajczac and J. -L. Pierro, *J. Org. Soc.*, **61**, 7452 (1996).

123. R. Ghorbani-Vaghei, H. Veisi and M. Amiri, *J. Chin. Chem. Soc.*, **54**, 1257 (2007); *Chem. Abstr.*, **147**, 142766 (2007).

124. A. Khazaei, A. Rostami and A. Aminimanesh, *J. Chin. Chem. Soc.*, **53**, 437 (2006); *Chem. Abstr.*, **145**, 248599 (2006).

125. A. Khazaei, M. A. Zolfigol and A. Rostami, *Synthesis*, 2959 (**2004**).

126. M. H. Ali, M. Hartman, K. Lamp, C. Schmitz and T. Wencewicz, *Synth. Commun.*, **36**, 1769 (2006).

127. K. Surenda, N. S. Krishnaveni, V. P. Kumar, R. Sridhar and K. R. Rao, *Tetrahedron Lett.*, **46**, 4581 (2005).

128. A. Khazaei, A. Aminmanesh and A. Rostami, *J. Chem. Res., (S)*, 391 (**2006**).

129. A. Khazaei and A. Rostami, *Phosphorus, Sulfur, and Silicon*, **180**, 555 (2005).

130. M. A. Zolfigol, D. Azarifar and B. Maleki, *Tetrahedron Lett*., **45**, 2181 (2004).

131. D. Azarifar and B. Maleki, *J. Chin. Chem. Soc.*, **52**, 1215 (2005); *Chem. Abstr.*, **145**, 230574 (2006).

132. I. Mohammadpoor-Baltork, M. A. Zolfigol and M. Abdollahi-Alibeik, *Synlett*, 2803 (**2004**).

133. M. A. Zolfigol, E. Madrakian, E. Ghaemi and S. Mallakpour, *Synlett*, 1633 (**2002**).

134. M. A. Zolfigol, R. Ghorbani-Vaghei, S. Mallakpour, G. Chehardoli, A. G. Choghamarani and A. Hosein-Yazdi, *Synthesis*, 1631 (**2006**).

135. M. A. Zolfigol, H. Nasr-Isfahani, S. Mallakpour and M. Safaiee, *Synlett*, 761 (**2005**).

136. R. Ghorbani-Vaghei, D. Azarifar and B. Maleki, *J. Chin. Chem. Soc.*, **51**, 1373 (2004); *Chem. Abstr.*, **142**, 430184e (2005).

137. R. Ghorbani-Vaghei, D. Azarifar, A. Khazaei and B. Maleki, *Phosphorus, Sulfur, and Silicon*, **179**, 1877 (2004).

138. R. Ghorbani-Vaghei, D. Azarifar and B. Maleki, *Bull. Korean Chem. Soc.*, **25**, 953 (2004); *Chem. Abstr.*, **141**, 260092h (2004).

139. D. Azarifar, E. Nademi, R. Ghorbani-Vaghei and B. Maleki, *Mendeleev Commun.*, 330 (**2006**).

140. K. I. Booker-Milburn, M. Fidouloff, S. J. Paknoham, J. B. Strachan, J. L. Melville and M. Voyle, *Tetrahedron Lett.*, **41**, 4657 (2000).

141. P. Froyen, *Synth. Commun.*, **25**, 959 (1995).

142. N. Iranpoor, H. Firouzabadi and G. Aghapour, *Synth. Commun.*, **32**, 2535 (2002).

143. M. Gucma and W. M. Gołębiewski,*Synthesis*, 1997 (**2008**).

144. M. Niu, H. Fu, Y. Jiang and Y. Zhaoa,*Synthesis*, 2879 (**2008**).

145. H. Firouzabadi, N. Iranpoor and F. Ebrahimzadeh, *Tetrahedron Lett.*, **47**, 1771 (2006).

146. Y. Wang and X. Liang, *Chinese J. Org. Chem.*, **25**, 969 (2005); *Chem. Abstr.*, **143**, 29969j (2006).

147. F. Chen, Y. Kuang, H. Dai, L. Lu and M. Huo, *Synthesis*, 2629 (**2003**).

148. G. A. Hieagl and M. Rubinho, *Synth. Commun.*, **32**, 2691 (2002).

149. G. F. Mendonca, A. M. Sansererino and M. C. S. De Mattos, *Synthesis*, 45 (**2002**).

150. G. A. Hieagl, C. D. Bayne and B. Reidly, *Synth. Commun.*, **33**, 1997 (2003).

151. G. A. Hiegel and T. J. ??, *Synth. Commun.*, **35**, 2091 (2005).

152. T. R. Walters, W. W. Zajac and J. M. Woods, *J. Org. Chem.*, **56**, 6748 (1991).

153. J. Jeko, T. Timar and J. Jaszberenyi, *J. Org. Chem.*, **56**, 6748 (1991).

154. R. Ghorbani-Vaghei, E. Shahbazi and H. Veisi, *Mendeleev Commun.*, 207 (**2005**).

155. R. Ghorbani-Vaghei and H. Veisi, *Synthesis*, 945 (**2009**).

156. M. A. Zolfigol, E. Ghaemi, E. Madrakian and A. Ghorbani-Choghamarani, *Mendeleev Commun.*, 41 (**2006**).

157. K. Niknam and M. A. Zolfigol, *J. Iran. Chem. Soc.*, **3**, 59 (2006); *Chem. Abstr.*, **145**, 505005 (2006). The N-nitrosation of amines with sodium nitrate and N-haloamines was reported much earlier by Anselme and his group [*Chem. Commun.*, 451 (**1984**) and *Tetrahedron Lett.*, **25**, 2619 (1984)].

158. A. Khazaei, A. Alizadeh and R. Ghorbani-Vaghei, *Molecules*, **6**, 253 (2001).

159. W. L. Collibee, M. Nakajima and J.-P. Anselme, *J. Org. Chem.*, **60**, 468 (1995).

160. L. S. Konstntinova, O. A. Rakitin, C. W. Rees, L. I. Souvorova and T. Torroba, *J. Chem. Soc., Perkin Trans.1.*, 1023 (**1999**).

161. J. D. Kreisberg, P. Magnus and S. Shinde, *Tetrahedron Lett.*, **43**, 7393 (2002).

162. H. Hazarkhani and B. Karimi, *Synthesis*, 1239 (**2004**).

163. G. D. K. Kumar and S. Baskaran, *Chem. Commun.*, 1026 (**2004**).

164. S. L. Ali, M. D. Nikalje and A. Sudalai, *Org. Lett.*, **1**, 705 (1999).

165. D. Kano, S. Minakata and M. Komatsu, *J. Chem. Soc. Perkin Trans. 1*, 3186 (**2001**).

166. H. Wu, L. W. Xu, C. G. Xia, J. Ge, W. Zhou and L. Yang, *Catal. Commun.*, **6**, 221 (2005).

167. S. L. Jain, J. K. Joseph and B. Sain, *J. Mol. Catal. A: Chem.*, **256**, 16 (2006).

168. V. V. Thakur and A. Sudalai, *Tetrahedron Lett.*, **44**, 989 (2003).

169. P. S. Aujla, C. P. Baird and P. C. Taylor, *Tetrahedron Lett.*, **38**, 7453 (1997).

170. I. Booker-Milburn, D. J. Guly, B. Cox and P. A. Procopiou, *Org. Lett.*, **5**, 3313 (2003).

171. F. Shirini, M. A. Zolfigol and E. Mollarazi,*Lett. Org. Chem.*, **2**, 398 (2005).

172. R. Ghorbani-Vaghei and H. Veisi, *J. Braz. Chem. Soc.*, **21**, 193 (2010); *Chem. Abstr.*, **153**, 85397 (2010).

173. R. Ghorbani-Vaghei and H. Veisi, *Mol. Divers.*, **14**, 249 (2010).

174. R. Ghorbani-Vaghei and H. Veisi, *S. Afr. J. Chem.*, **62**, 33 (2009); *Chem. Abstr.*, **151**, 288894 (2009).